



# PCCP

## Reaction pathways for HCN on transition metal surfaces

Journal:	<i>Physical Chemistry Chemical Physics</i>
Manuscript ID	CP-ART-12-2018-007548.R1
Article Type:	Paper
Date Submitted by the Author:	19-Jan-2019
Complete List of Authors:	Abdel-Rahman, Mohammed; University of Illinois at Chicago, Chemistry Feng, Xu; Virginia Polytechnic Institute and State University, 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

SCHOLARONE™  
Manuscripts



Journal Name

ARTICLE

## Reaction pathways for HCN on transition metal surfaces

Mohammed Abdel-Rahman<sup>a</sup>, Xu Feng<sup>a</sup>, Mark Muir<sup>a</sup>, Kushal Ghale<sup>b</sup>, Ye Xu<sup>b</sup>, and Michael Trenary<sup>\*a</sup>

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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  $\nu(\text{C-H})$  stretch peak at  $\sim 3300 \text{ cm}^{-1}$ , 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 aminocarbene species,  $\text{CNH}_2$ , which was also observed on the Pt(111) surface. DFT calculations confirm the high stability of  $\text{CNH}_2$  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  $1540 \text{ cm}^{-1}$  following HCN adsorption on Pd(111) at 300 K.<sup>1, 2</sup> This frequency is characteristic of a C=N double bond from which they concluded that HCN bonds to the surface in a di- $\sigma$  configuration with the C=N bond parallel to the surface. A NEXAFS study confirmed this orientation for the CN bond.<sup>1</sup>

In a series of papers<sup>3-8</sup>, 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 adsorbed molecule to that of gas phase HCN. In particular, the CH stretch of HCN on Pt(111) was observed at  $3298\text{-}3000 \text{ cm}^{-1}$ , compared to values of  $3311\text{-}3312 \text{ cm}^{-1}$  in the gas phase<sup>9, 10</sup> and  $3305\text{-}3306 \text{ cm}^{-1}$  in an argon matrix.<sup>11, 12</sup> 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  $712 \text{ cm}^{-1}$  in the gas phase<sup>9, 10</sup>, which was below the low wavenumber cut-off in our RAIRS studies. However, we detected a peak at  $1311 \text{ cm}^{-1}$  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  $1323 \text{ cm}^{-1}$ , which were assigned to an  $\text{NH}_2$  symmetric stretch, a  $\text{NH}_2$  scissor mode, and a C=N stretch, respectively, of an aminocarbene ( $\text{CNH}_2$ ) species.<sup>3</sup> These assignments were supported by observing isotopic shifts after adsorbing  $\text{H}^{13}\text{C}^{14}\text{N}$  and  $\text{H}^{12}\text{C}^{15}\text{N}$ . Subsequent density

<sup>a</sup> Department of Chemistry, University of Illinois at Chicago, 845 W Taylor Street, Chicago, IL 60607 USA.

<sup>b</sup> 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).<sup>13</sup> 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.<sup>14, 15</sup> In independent work, aminocarbyne has also been identified as a stable intermediate on R(111) in the decomposition of methyl amine<sup>16</sup> and azomethane.<sup>17</sup>

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<sub>2</sub>. 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 <sup>13</sup>C and <sup>15</sup>N substitution, we show that CNH<sub>2</sub> does indeed form on Pd(111). Furthermore, our DFT calculations suggest that CNH<sub>2</sub> 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 programmed 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.<sup>18</sup> 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.<sup>19</sup>

Hydrogen cyanide was synthesized using the method of Hagans et al. in which potassium cyanide was reacted with H<sub>2</sub>SO<sub>4</sub>(aq).<sup>20</sup> Natural abundance KCN was purchased from Aldrich Chemical Company with a quoted purity of 97%. H<sup>13</sup>C<sup>14</sup>N and H<sup>12</sup>C<sup>15</sup>N were synthesized using the same procedure with K<sup>13</sup>C<sup>14</sup>N and K<sup>12</sup>C<sup>15</sup>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<sup>21</sup>) with the optB86b Van der Waals (vdW) functional developed by Klimeš et al.<sup>22, 23</sup> as well as the GGA-RPBE functional<sup>24</sup> for comparison. Core electrons were described by the projector augmented wave (PAW) method<sup>25, 26</sup> 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.<sup>27</sup> 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<sup>28</sup>). 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<sup>29</sup>. 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<sup>30</sup> and the dimer method.<sup>31</sup> The activation energy was calculated as  $E_a = E_{\text{TS}} - E_{\text{IS}}$ , 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.<sup>32</sup> 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.<sup>32</sup> 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 ( $\nu_i$ ) of a molecule as:

$$E^{ZPE} = \frac{1}{2} \sum_i \hbar \omega_i$$

## 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)<sup>6</sup>. For the highest exposures, HCN forms a multilayer and the spectra are similar to those reported previously for solid HCN.<sup>33-36</sup> 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<sup>-1</sup> 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<sup>-1</sup> after

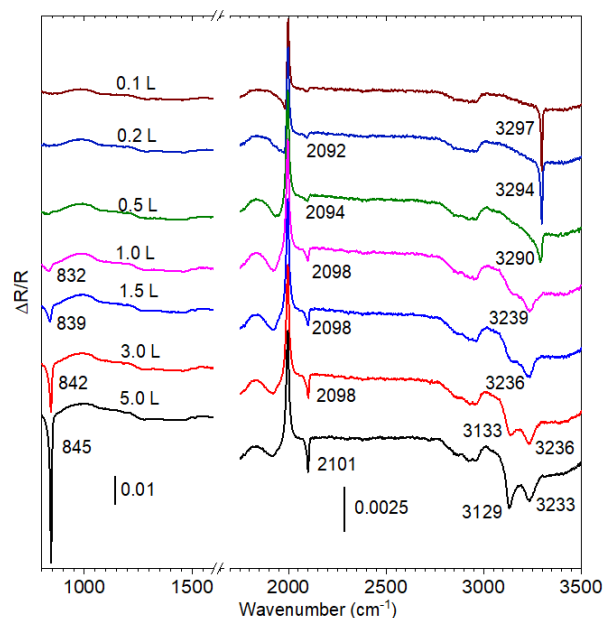


Figure 1. RAIR spectra for increasing exposures of HCN to Ru(001) at 90 K. The negative peak just below 2000 cm<sup>-1</sup> is due to adsorbed CO that is displaced and shifted upon HCN adsorption.

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<sup>-1</sup> is by far the most intense. The CN stretch, seen at 2101 cm<sup>-1</sup> 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<sup>-1</sup> is close to the value of gas phase HCN<sup>9</sup> at 3312 and of HCN in an Ar matrix<sup>11, 12</sup> at 3305-3306 cm<sup>-1</sup>. 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

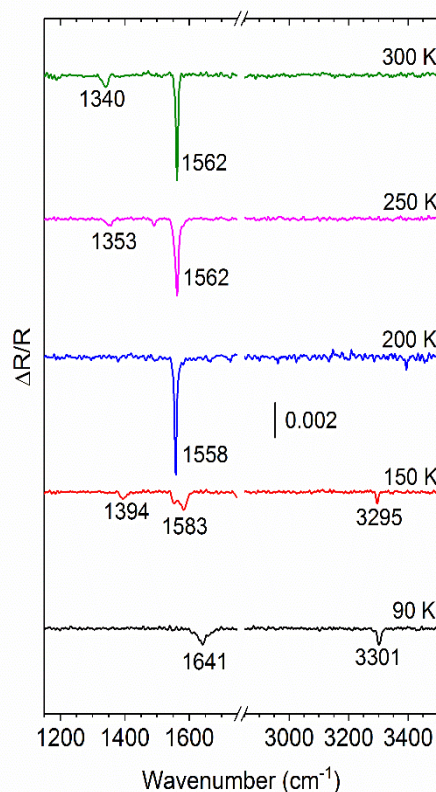


Figure 2. RAIR spectra of H<sup>12</sup>C<sup>14</sup>N after exposure of 1.0 L to Pd(111) and annealing to the indicated temperatures. These spectra were obtained with 4096 scans, corresponding to approximately 16 minutes per spectrum.

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<sup>-1</sup> on Pt(111)<sup>3, 6</sup> and at 1395 on Cu(100).<sup>6</sup> 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<sup>12</sup>C<sup>14</sup>N, two peaks are seen at 1641 and 3301 cm<sup>-1</sup>. 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.

The assignment of the peak at  $1641\text{ cm}^{-1}$  is less straightforward. In solid HCN<sup>33-35</sup>, the overtone of the bending mode occurs at  $1621\text{--}1632\text{ cm}^{-1}$  whereas it is at  $1427\text{ cm}^{-1}$  in an Ar matrix<sup>12</sup> and at  $1412\text{ cm}^{-1}$  in gas phase HCN.<sup>37</sup> For HCN on Pt(111) and Cu(100), we assigned peaks at  $1311$  and  $1395\text{ cm}^{-1}$  to the bending overtone.<sup>3, 6</sup> The peak observed at  $1641\text{ cm}^{-1}$  in Fig. 2 could be plausibly assigned to the bending overtone, but this frequency is also consistent with a CN double bond

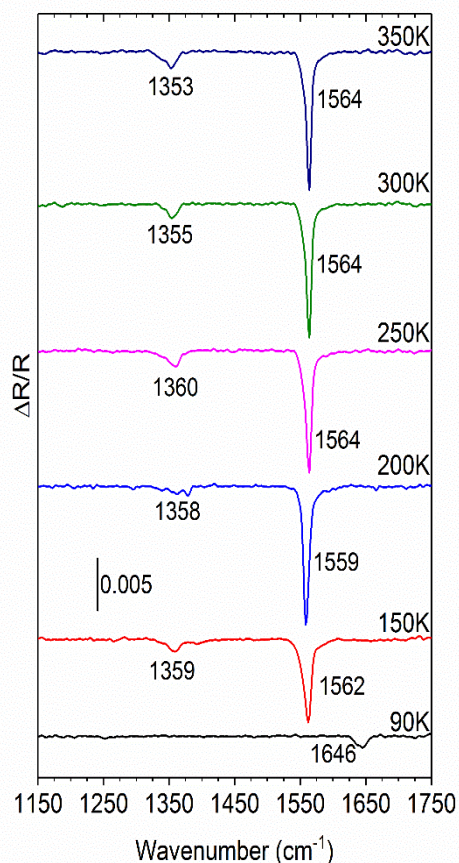


Fig. 3. RAIR spectra of  $1.0\text{ L H}^{12}\text{C}^{14}\text{N}$  taken at  $90\text{ K}$  after annealing for one minute at the indicated temperatures.

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  $\text{CNH}_2$  on Pt(111) upon substitution with  $^{13}\text{C}$  and  $^{15}\text{N}$  along with the ratio of the shifted frequencies. As the values of the bending overtone for the  $^{13}\text{C}$  and  $^{15}\text{N}$  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.<sup>10</sup> With ratios of  $0.9872$  and

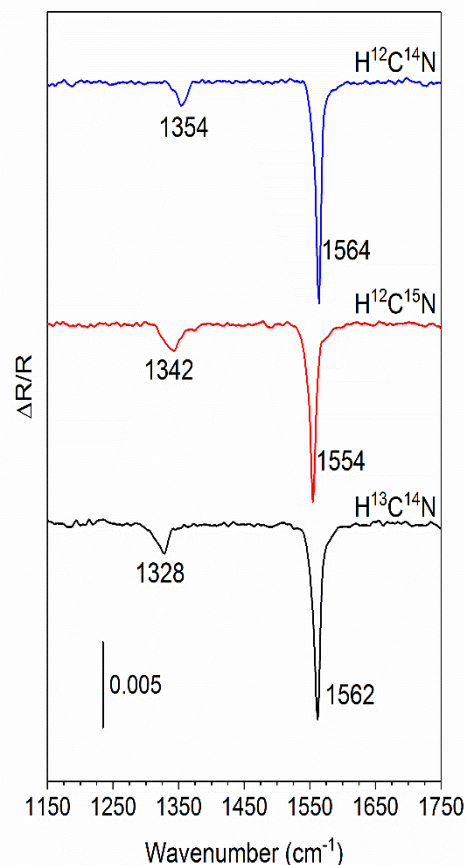


Fig. 4. A comparison of RAIR spectra taken at  $90\text{ K}$  for each isotope after annealing at  $300\text{ K}$  for one minute.

$0.9884$  upon  $^{13}\text{C}$  and  $^{15}\text{N}$  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  $1311\text{ cm}^{-1}$ ). Moreover, these shifts are notably different from what is seen for the CN bond stretch of gas phase HCN or of  $\text{CNH}_2$  on Pt(111), where the bond-order is between one and two. We therefore assign the  $1641\text{ cm}^{-1}$  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  $1641\text{ cm}^{-1}$  is consistent with a C=N stretch, a C=N double bond implying  $\text{sp}^2$  hybridization on the carbon atom is not consistent with the high value of the CH stretch peak at  $3301\text{ cm}^{-1}$ .

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

	$\text{H}^{12}\text{C}^{14}\text{N}$	$\text{H}^{13}\text{C}^{14}\text{N}$	$\text{H}^{12}\text{C}^{15}\text{N}$
$\delta(\text{HCN})$ , Ar matrix <sup>11</sup>	721	715 (0.9917)	720 (0.9986)
$2\times\delta(\text{HCN})$ , Ar matrix <sup>11</sup>	1442	1430 (0.9917)	1440 (0.9986)
$\nu(\text{CN})$ , gas <sup>10</sup>	2097	2063 (0.9838)	2064 (0.9838)
$2\times\delta(\text{HCN})$ , Pt(111) <sup>3</sup>	1311	1295 (0.9878)	1303 (0.9939)
$2\times\delta(\text{HCN})$ , Pd(111)	1641	1620 (0.9872)	1622 (0.9884)
$\nu(\text{CN})$ , $\text{CNH}_2$ Pt(111) <sup>3</sup>	1323	1290 (0.9751)	1312 (0.9917)

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  $1562\text{ cm}^{-1}$  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  $3295\text{ cm}^{-1}$ . 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 miscancellations 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  $3400\text{ cm}^{-1}$  in the 200 K spectrum and  $1500\text{ cm}^{-1}$  in the 250 K spectrum, are not.

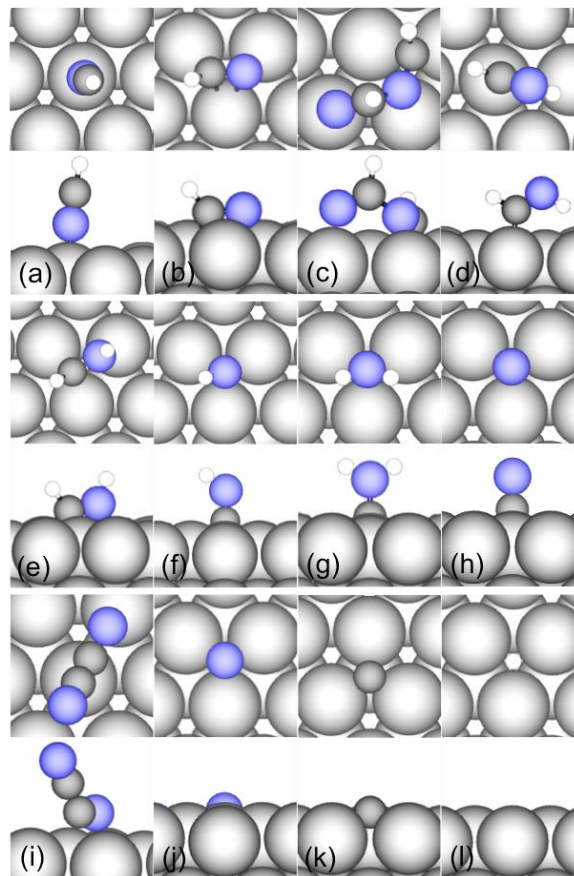
**Table 2.** Peak positions for the  $\nu(\text{CN})$  and  $\delta(\text{NH}_2)$  modes of  $\text{CNH}_2$  on Pd(111) (experimental and calculated) and Pt(111) (experimental) and ratios, in parentheses, of the positions relative to those of  $^{12}\text{C}^{14}\text{NH}_2$ .

Mode, Isotopologue	Pd(111) (exp.)	Pd(111) (calc.)	Pt(111) (exp.)
$\nu(\text{CN})$ , $^{12}\text{C}^{14}\text{NH}_2$	1354	1347	1323
$\nu(\text{CN})$ , $^{13}\text{C}^{14}\text{NH}_2$	1328 (0.9808)	1317 (0.9777)	1290 (0.9751)
$\nu(\text{CN})$ , $^{12}\text{C}^{15}\text{NH}_2$	1342 (0.9911)	1337 (0.9926)	1312 (0.9917)
$\delta(\text{NH}_2)$ , $^{2}\text{C}^{14}\text{NH}_2$	1564	1524	1567
$\delta(\text{NH}_2)$ , $^{3}\text{C}^{14}\text{NH}_2$	1562 (0.9987)	1521 (0.9980)	1566 (0.9994)
$\delta(\text{NH}_2)$ , $^{2}\text{C}^{15}\text{NH}_2$	1554 (0.9936)	1514 (0.9934)	1559 (0.9949)

The most significant changes occur in the lower wavenumber range and Fig. 3 shows spectra from  $1150$  to  $1750\text{ cm}^{-1}$ , 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  $1646\text{ cm}^{-1}$  peak to disappear and be replaced by peaks at  $1562$  and  $1359\text{ cm}^{-1}$ . The  $1359\text{ cm}^{-1}$  peak is accompanied by a weak feature at about  $1390\text{ cm}^{-1}$  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  $\text{CNH}_2$ . The spectra show little change from 200 to 350 K, demonstrating the stability of  $\text{CNH}_2$  on the Pd(111) surface.

The assignment of the  $\text{CNH}_2$  peaks seen in Fig. 3 is aided by repeating the experiment with  $\text{H}^{13}\text{C}^{14}\text{N}$  and  $\text{H}^{12}\text{C}^{15}\text{N}$  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  $\text{H}^{12}\text{C}^{14}\text{N}$ ,  $\text{H}^{13}\text{C}^{14}\text{N}$  and  $\text{H}^{12}\text{C}^{15}\text{N}$ . Table 2 lists the wavenumber values for

the  $\nu(\text{CN})$  and  $\delta(\text{NH}_2)$  modes for  $\text{CNH}_2$  on Pd(111) along with the corresponding values for  $\text{CNH}_2$  on Pt(111). The fact that the peak at  $1564\text{ cm}^{-1}$  shifts to  $1554$  upon  $^{15}\text{N}$  substitution but to only  $1562\text{ cm}^{-1}$  with  $^{13}\text{C}$  substitution clearly reveals that this is a  $\delta(\text{NH}_2)$  mode, rather than a C=N stretch. The large shift of the peak at  $1354$  to  $1342\text{ cm}^{-1}$  with  $^{15}\text{N}$  substitution and to  $1328\text{ cm}^{-1}$  with  $^{13}\text{C}$  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 ( $\text{CNH}_2$ ), forms on both surfaces.

**Fig. 5.** DFT (optB86b-vdW) calculated minimum-energy adsorption configurations for (a) upright HCN; (b) di- $\sigma$  HCN; (c)  $(\text{HCN})_2$ ; (d) trans-HCNH; (e) cis-HCNH; (f) CNH; (g)  $\text{CNH}_2$ ; (h) CN; (i)  $(\text{CN})_2$ ; (j) N; (k) C; (l) H. In each panel, the top view is shown on top and the side view is shown on bottom. Silver, blue, black, and white spheres represent Pd, N, C, and H atoms, respectively. Periodic images of the adsorbates have been removed for clarity.

## 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 ( $\Delta E_{\text{ads}}$ ) 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.<sup>38</sup>

The preferred adsorption sites of several of the species, including di- $\sigma$  HCN, CN, and atomic H, are consistent with those previously reported by Herron et al.<sup>39</sup> CN, CNH, and CNH<sub>2</sub> 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.<sup>1</sup> 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.<sup>40</sup> *Cis*- and *trans*-HCNH are included as potential intermediates to CNH<sub>2</sub>. 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.<sup>41</sup> finds that the contribution of vdW energies to adsorption on transition metal surfaces becomes significant when the values of RPBE  $\Delta E_{\text{ads}}$  fall roughly below 70% of the corresponding ones for optB86b.<sup>41</sup> 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 ( $\Delta E_{\text{ads}}$ , in eV) of various molecular and atomic intermediates in HCN decomposition on Pd(111), in comparison with available DFT and experimental literature values.

Species	Preferred site	$\Delta E_{\text{ads}}$		DFT lit. <sup>1</sup>	Exp. lit.
		GGA-RPBE	optB86b-vdW		
HCN upright	top	0.00	-0.56		-0.39 <sup>2</sup>
HCN di- $\sigma$	top-top   br-br	-0.47	-1.29	-0.42	
(HCN) <sub>2</sub> <sup><math>\alpha</math></sup>	top-top-br	-0.15 <sup>3</sup>	-1.02 <sup>3</sup>		
HCNH <i>trans</i>	top	-1.75	-2.49		
HCNH <i>cis</i>	br-top	-2.21	-3.21		
CNH	fcc	-1.69	-2.40		
CNH <sub>2</sub>	fcc	-3.57	-4.48		
CN	fcc	-3.33	-4.08	-3.25	
(CN) <sub>2</sub>	top-top	-3.11 <sup>3</sup>	-3.78 <sup>3</sup>		
C	hcp	-6.40	-6.99	-5.80	
N	fcc	-4.29	-5.03	-3.55	
H	fcc	-2.69	-3.06	-2.69	-2.80 <sup>4</sup>

Each adsorbate is located on a (2×2) surface unit cell at 1/4 ML coverage.  $\Delta E_{\text{ads}}$  is with respect to each adsorbate in gas phase and is non-ZPE corrected. "br" stands for bridge site.

<sup>1</sup> From Ref. <sup>39</sup>

<sup>2</sup> From Ref. <sup>42</sup>

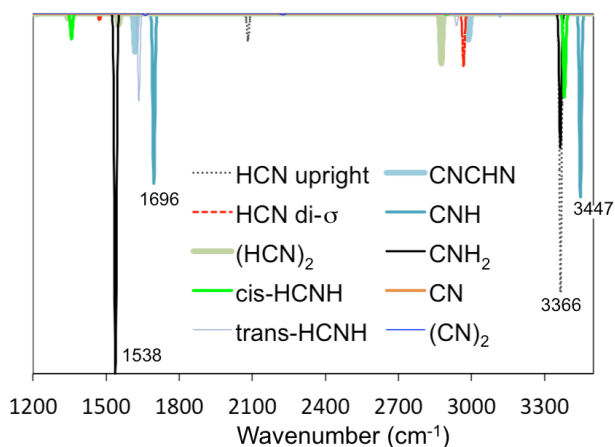
<sup>3</sup> per unit of HCN or CN.

<sup>4</sup> From Ref. <sup>43</sup>

Thus the low-temperature HCN desorption features observed by Guo et al.,<sup>42</sup> 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  $\Delta E_{\text{ads}}$  of -0.56 eV (-13 kcal/mol) for upright HCN. The subsequent investigation of the decomposition pathway is conducted based on the optB86b results.

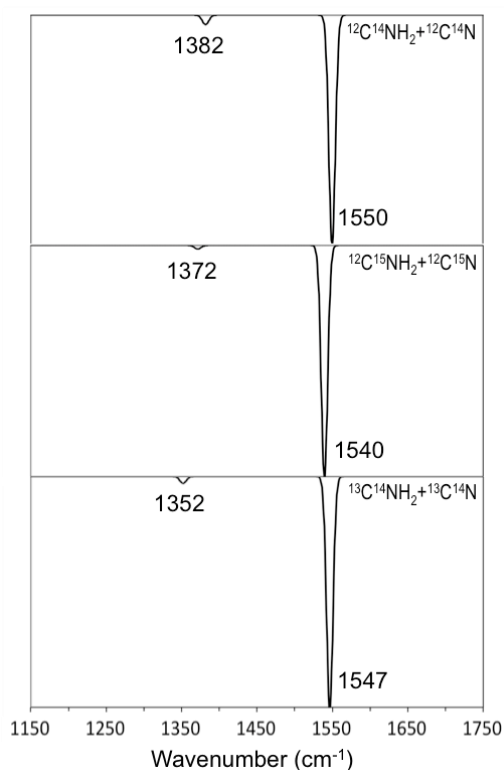
#### 4.2.2 Simulated infrared spectra of intermediates

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  $CNH_2$  ( $1538\text{ cm}^{-1}$ ) and the



**Fig. 6.** DFT (optB86b-vdW) calculated IR spectra of possible molecular intermediates formed upon adsorption of HCN on Pd(111). All intermediates calculated at 1/4 ML coverage without any co-adsorbate.

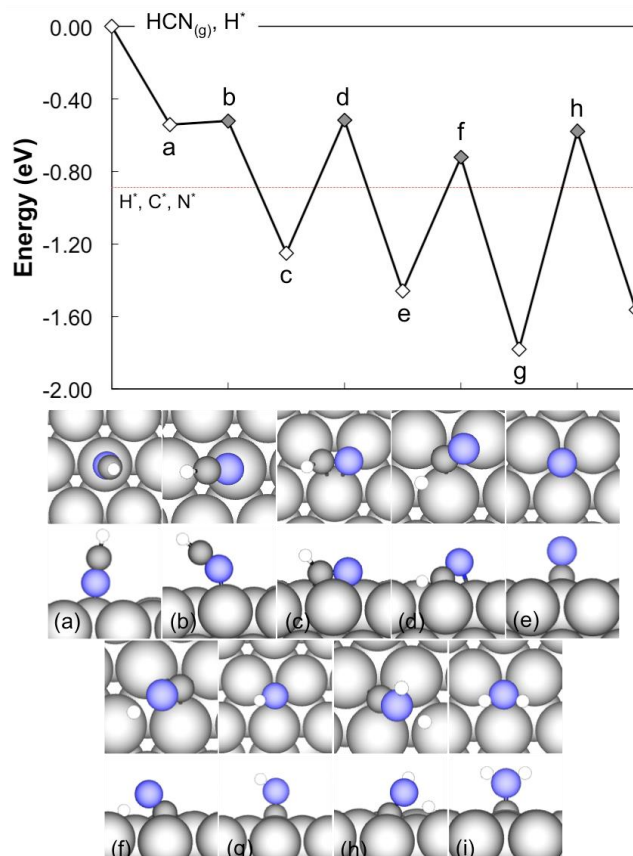
$\nu(CH)$  mode of upright HCN ( $3366\text{ cm}^{-1}$ ). They are in line with the assignment of  $1564\text{ cm}^{-1}$  to  $CNH_2$  and  $3301\text{ cm}^{-1}$  to HCN. Di- $\sigma$  HCN is expected to be essentially undetectable with RAIRS due to the lack of any strong mode. CNH, and *cis*- and *trans*-HCNH have several modes with moderate IR intensities. The  $\nu(CN)$  mode of adsorbed CN is calculated to have a very weak



**Fig. 7.** DFT (optB86b-vdW) calculated IR spectra of normal and isotopically labelled  $CNH_2$  on Pd(111).  $CNH_2$  (in fcc site) is coadsorbed with CN (in hcp site), for an overall coverage of 1/2 ML.

intensity and a frequency of  $1922\text{ cm}^{-1}$ , in agreement with the HREELS assignment of  $1910\text{ cm}^{-1}$  by Kordesch et al. to  $CN$ .<sup>1</sup>

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



**Fig. 8.** (Upper) DFT (optB86b-vdW) calculated reaction energy profile for uni-molecular HCN decomposition on Pd(111) at 1/4 ML coverage. (a) upright HCN, (b) isomerization TS; (c) di- $\sigma$  HCN; (d) dehydrogenation TS; (e) CN; (f) hydrogenation TS; (g) CNH; (h) hydrogenation TS; (i)  $CNH_2$ . “†” indicates a transition state (TS). Zero on the y-axis corresponds to a gas phase HCN molecule and an H atom adsorbed on surface. Horizontal line corresponds to atomic H, C, and N (i.e. atomized HCN) at infinite separation from one another. Energies are ZPE-corrected DFT total energies. For brevity, balance of H atoms (at infinite separation) is not indicated. (Lower) Snapshots of the surface intermediates and transition states, with top views on top and side views on bottom. Labels correspond to those in the upper panel. Silver, blue, black, and white spheres represent Pd, N, C, and H atoms, respectively.

$\nu(CN)$  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  $1564\text{ cm}^{-1}$  and  $1354\text{ cm}^{-1}$  (Fig. 4) to  $CNH_2$ .

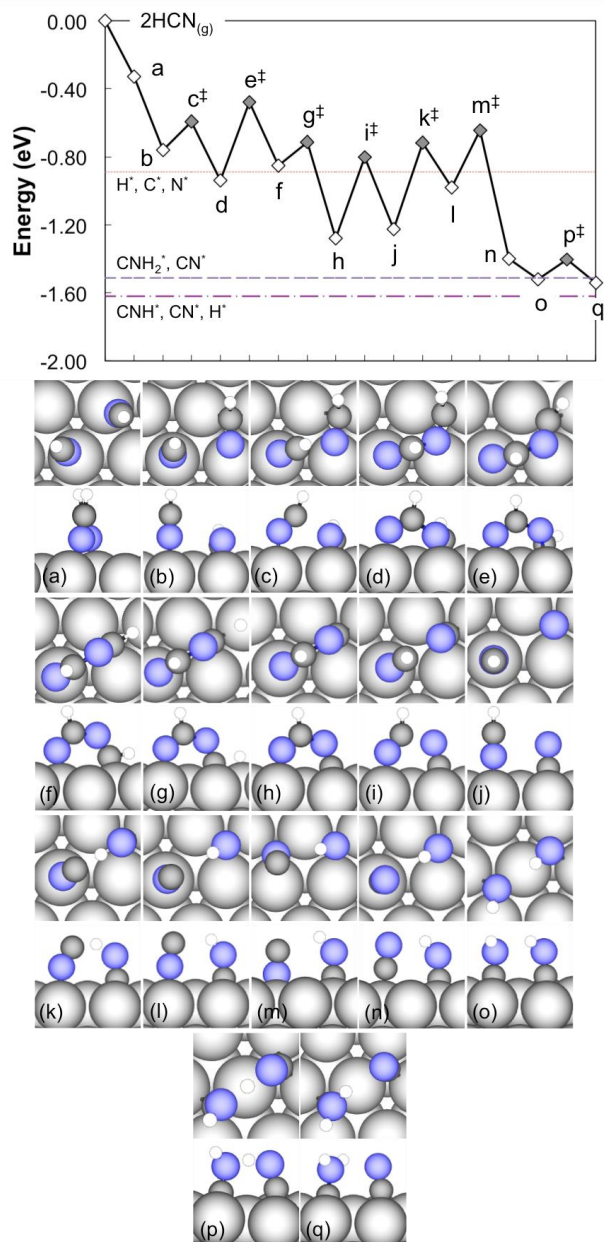
#### 4.2.3 Reaction pathways for HCN decomposition on Pd(111)

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  $\text{CNH}_2$  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 optB86b, is predicted to convert to the di- $\sigma$  state with an



**Fig. 9.** (Upper) DFT (optB86b-vdw) calculated reaction energy profile for bi-molecular HCN decomposition on Pd(111) at combined 1/2 ML coverage. (a) 2 upright HCN, (b) 1 upright HCN and 1 di- $\sigma$  HCN; (c) dimerization TS; (d)  $(\text{HCN})_2^{\alpha}$ ; (e) isomerization TS; (f)  $(\text{HCN})_2^{\beta}$ ; (g) dehydrogenation TS; (h) CNCHN; (i) C-N scission TS; (j) HCN and CN; (k) H transfer TS; (l) NC and CNH; (m) flipping TS; (n) CN and CNH; (o) 2 CNH; (p) H transfer TS; (q)  $\text{CNH}_2$  and CN. “ $\ddagger$ ” indicates a transition state (TS). Zero on the y-axis corresponds to a gas phase HCN molecule and an H atom adsorbed on surface. Horizontal lines correspond to indicated surface species at infinite separation from one another. Energies are ZPE-corrected DFT total energies. For brevity, balance of H atoms (at infinite separation) is not indicated. (Lower) Snapshots of the surface intermediates and transition states, with top views on top and side views on bottom. Labels correspond to those in the upper panel. Silver, blue, black, and white spheres represent Pd, N, C, and H atoms, respectively.

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.

**Table 4:** Optb86b-vdW calculated forward activation energies ( $E_a$ , in eV), reaction energies ( $\Delta E$ , in eV)<sup>#</sup> in the minimum energy uni-molecular mechanism.

Step	$E_a$	$\Delta E$	$E_a^{\text{ZPE}}$	$\Delta E^{\text{ZPE}}$
1. $\text{HCN}^{\text{upright}} \rightarrow \text{HCN}^{\text{di-}\sigma}$	0.01	-0.73	0.00	-0.71
2. $\text{HCN} \rightarrow \text{CN} + \text{H}$	0.93	-0.07	0.74	-0.21
3. $\text{CN} + \text{H} \rightarrow \text{CNH}$	0.79	-0.44	0.74	-0.32
4. $\text{CNH} + \text{H} \rightarrow \text{CNH}_2$	1.23	+0.03	1.20	+0.21

<sup>#</sup>  $\Delta E$  calculated with species at infinite separation.

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  $\text{CNH}_2$  formation on Pt(111).<sup>15</sup> 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  $\text{CNH}_2$  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.<sup>44</sup> 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  $1032 \text{ cm}^{-1}$ , 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  $\text{CNH}_2$  formation.

Alternatively, we have explored whether bi-molecular interaction can facilitate the formation of  $\text{CNH}_2$ , 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- $\sigma$  HCN, yielding a dimer state  $(\text{HCN})_2^{\alpha}$ . 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, below the negative of the  $\Delta E_{\text{ads}}$  of the upright HCN state. After structural rearrangement, the dimer state  $(\text{HCN})_2^{\beta}$  undergoes dehydrogenation with a low activation energy of 0.14 eV. The remaining fragment, CNCHN, then undergoes an intramolecular CN bond scission to produce a CN group and an upright HCN. An intermolecular H transfer between the two

species yields a CNH and a NC group binding through the N atom to a top site. The NC species is significantly less stable than the CN group, and it undergoes rapid conversion to the latter through a flipping movement. Finally, two CNH molecules undergo another intermolecular H transfer to produce CNH<sub>2</sub> and CN. The highest kinetic barrier is 0.51 eV

**Table 5:** OptB86b-vdW calculated forward activation energies ( $E_a$ , in eV), reaction energies ( $\Delta E$ , in eV per unit of HCN)<sup>#</sup> in the minimum energy bimolecular mechanism.

Step	$E_a$	$\Delta E$	$E_a^{ZPE}$	$\Delta E^{ZPE}$
1. 2HCN $\rightarrow$ (HCN) <sub>2</sub> <sup>α</sup>	0.17	-0.23	0.17	-0.18
2. (HCN) <sub>2</sub> <sup>α</sup> $\rightarrow$ (HCN) <sub>2</sub> <sup>β</sup>	0.53	+0.10	0.46	+0.09
3. (HCN) <sub>2</sub> <sup>β</sup> $\rightarrow$ CNCHN+H	0.25	-0.38	0.14	-0.43
4. CNCHN $\rightarrow$ CN+HCN	0.56	+0.10	0.48	+0.06
5. CN+HCN $\rightarrow$ CNH+NC	0.61	+0.25	0.51	+0.24
6. CNH+NC $\rightarrow$ CNH+CN	0.35	-0.43	0.34	-0.42
7. 2CNH $\rightarrow$ CNH <sub>2</sub> + CN <sup>†</sup>	0.20	-0.04	0.11	-0.02

<sup>#</sup>  $\Delta E$  calculated with organic species co-adsorbed in same (2×2) surface unit cell. Balance of H is placed at infinite separation.

<sup>†</sup>  $\Delta E$  calculated with balance of CN and H at infinite separation.

(Step 5), which is much more in line with the observed low-temperature reactivity of HCN. Due to the involvement of upright HCN, a locally high coverage would be required to stabilize the state, which implies that this mechanism would not be operative at very low initial HCN coverages. We have used the approach by Herron et al.<sup>39</sup> to estimate the diffusion barriers for upright and di- $\sigma$  HCN. Both are estimated to be less than 0.1 eV, indicating that surface mobility does not preclude adsorbed HCN molecules from finding and reacting with one another on Pd(111).

**Table 6:** OptB86b-vdW calculated energies (in eV) for several possible states of HCN on Cu(100), Pd(111), and Ru(001).

State	Cu(100)	Pd(111)	Ru(001)
upright HCN	-0.32	-0.54	-0.91
di- $\sigma$ HCN	-0.79	-1.25	-2.05
CN+H	-1.17	-1.46	-2.20
CNH <sub>2</sub>	-0.83	-1.57	-1.80
all atoms	+0.04	-0.89	-2.80

Energy is referenced to a clean surface, gas phase HCN, and an adsorbed H atom and is calculated on (2×2) surface unit cells. CN prefers a di- $\sigma$  geometry with the C-N bond axis parallel to the surface on Cu(100) and Ru(001). Multiple species in the same state are calculated at infinite separation.

The pathway produces coadsorbed CNH<sub>2</sub> 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  $2 \times \Delta E = -0.04$  eV). On an isolated basis, as indicated by the dashed lines in Fig. 9, CNH is more stable than CNH<sub>2</sub> (by 0.11 eV, or 0.18 eV with RPBE). Thus, although DFT predicts CNH<sub>2</sub> to be a stable product, it is not predicted to be overwhelmingly more stable than CNH. This is potentially a significant discrepancy with experiment, which finds no vibrational signature attributable to CNH on Pd(111). Whether this is due to any intrinsic error of DFT requires further investigation.

In any case, this mechanism predicts that following the formation of CNH<sub>2</sub>, the surface has a significant amount of CN and atomic H coexisting with CNH<sub>2</sub> since for every CNH<sub>2</sub>, 3 CN molecules and 2 H atoms are formed. The presence of excess H atoms on the surface is consistent with the TPD findings of Guo et al.,<sup>42</sup> who reported a H<sub>2</sub> desorption peak ca. 300 K that resembles the 2<sup>nd</sup> order desorption of pure hydrogen from Pd(111).<sup>45</sup>

We have also calculated the energy of adsorbed atomic H, C, and N (representing the complete atomization of HCN), which are less stable than di- $\sigma$  HCN, CN, CNH, and CNH<sub>2</sub> (Fig. 8), indicating that thermodynamics does not favour complete dissociation of HCN on Pd(111), which is indeed not observed experimentally. To shed light on the fate of HCN on Ru(001) and Cu(100), we compare the energies of several possible states, including upright and di- $\sigma$  HCN, CN+H, CNH<sub>2</sub>, and all atoms on Pd(111), Ru(001), and Cu(100) in Table 6. The energies for the species on Pd(111) are those plotted in Figure 8. On Ru(001) the completely atomized state has by far the lowest energy, at -2.80 eV, which suggests a significant driving force toward atomization on Ru(001) and is consistent with the fact that only upright HCN is observed on Ru(001). On Cu(100) thermodynamics favours CN+H. Whether HCN dissociation is kinetically more facile than HCN desorption will be the subject of a future study. We note that H<sub>2</sub> desorption is known to occur at lower temperature on Cu(100)<sup>46</sup> than on Pd(111). Thus monitoring H<sub>2</sub> 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 CNH<sub>2</sub> 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.<sup>2</sup> For a 0.1 L HCN exposure to Pd(111) at 300 K, loss peaks were observed at 1290 and 1540 cm<sup>-1</sup>, which given the HREELS resolution of 65 cm<sup>-1</sup>, are close to our values of 1354 and 1564 cm<sup>-1</sup>. 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<sup>-1</sup> peak to a C=N stretch and the 1290 cm<sup>-1</sup> 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<sup>-1</sup>.<sup>1</sup> These values are essentially at the same position, within the margin of error, as the peaks that we observe at 1354 and 1564 cm<sup>-1</sup> and assign to the  $\delta(\text{NH}_2)$  and  $\nu(\text{CN})$  modes of CNH<sub>2</sub>. We therefore conclude that the 300 K HREELS data is better assigned to CNH<sub>2</sub> than to a di- $\sigma$  bonded HCN species. Other earlier observations are also consistent with CNH<sub>2</sub> on Pd(111). For example, it was noted that the same spectra were obtained from HCN absorption as from the hydrogenation of CN produced from the dissociation of cyanogen.<sup>47</sup> On Pt(111), we showed that CN produced from cyanogen dissociation is

readily hydrogenated to  $\text{CNH}_2$ , and it follows that the same reaction occurs on Pd(111).<sup>48</sup>

The orientation of the CN bond of the proposed di- $\sigma$  bonded HCN was investigated with NEXAFS and the data indicated that the CN bond was parallel to the surface.<sup>1</sup> For the adsorbed diatomic molecules CO, NO, and CN, the NEXAFS spectra at the N 1s edge show a sharp  $\pi$  resonance at the threshold and a broader  $\sigma$  resonance at higher photon energy. The  $\sigma/\pi$  intensity ratio depends on the angle ( $\theta_E$ ) 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  $\text{CNH}_2$  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  $\text{CNH}_2$ . The calculations imply that di- $\sigma$  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.<sup>49</sup> Spectra obtained after annealing to 200 K an HCN layer adsorbed at 110 K should have produced a mixture of CN and  $\text{CNH}_2$ . 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 a di- $\sigma$  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 a thorough study of the reaction chemistry of HCN on Pd(111) as studied with TPRS by Guo et al.<sup>42</sup> Following an HCN exposure of  $2.6 \times 10^{15}$  molecules/cm<sup>2</sup> at a surface temperature of 87 K, three desorption products were observed: HCN,  $\text{H}_2$ , and  $\text{C}_2\text{N}_2$ . 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 ( $\alpha_3$ ) at 150 K. A single higher temperature HCN desorption peak ( $\beta_1$ ) was observed at 400 K. The latter was accompanied by reaction limited  $\text{H}_2$  desorption ( $\beta_2$ ). A desorption-limited  $\text{H}_2$  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.,<sup>42</sup> 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  $(\text{HCN})_x$  polymeric

species.<sup>42</sup> Upon heating,  $(\text{HCN})_x$  decomposes to liberate HCN ( $\beta_2$  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  $\beta_2$   $\text{H}_2$  peaks observed by Guo et al.<sup>42</sup> We can associate the  $\beta_1$   $\text{H}_2$  peak with the decomposition of the  $(\text{HCN})_2$  <sup>$\beta$</sup>  dimer to produce  $\text{CNCHN} + \text{H}$ , with the H atom stable on the surface until the recombinative  $\text{H}_2$  desorption temperature is reached. Guo et al.<sup>42</sup> found that for the lowest exposures to the Pd(111) crystal at 300 K,  $\beta_2$   $\text{H}_2$  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  $\text{CNH}_2$  for annealing temperatures above 300 K, the simplest conclusion is that  $\beta_1$  HCN and  $\beta_2$   $\text{H}_2$  are associated with  $\text{CNH}_2$  decomposition. We further assume that at low coverages,  $\text{CNH}_2$  decomposes by the reverse of the unimolecular mechanism to produce H, which immediately desorbs as  $\beta_2$   $\text{H}_2$ , 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  $\beta_2$   $\text{H}_2$  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- $\sigma$  bonded HCN (Fig. 9). This is only consistent with the experimental RAIRS results if we assume that the peaks of di- $\sigma$  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<sup>-1</sup>, the intensity of which rose and fell as HCN was converted to  $\text{CNH}_2$ , and was therefore attributed to the NH stretch 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<sup>-1</sup> peak fell between that of the CH stretch of adsorbed HCN and the NH stretch of  $\text{CNH}_2$ , whereas DFT implies that the NH stretch of CNH would lie above the NH stretch of  $\text{CNH}_2$ . Coincidentally, the NH stretch of  $\text{CNH}_2$  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<sup>-1</sup>. 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, demonstrate that CNH<sub>2</sub> forms on Pd(111). The RAIR spectra of CNH<sub>2</sub> on Pd(111) are almost identical to the spectra on Pt(111). The DFT calculations indicate that a bi-molecular mechanism for formation of CNH<sub>2</sub> from HCN with low barriers is available that can explain the observation of CNH<sub>2</sub> 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.

## Acknowledgements

We thank Ravi Ranjan, Hamzzat Soyege, and Jonathon Kruppe for assistance with the experiments. The experimental work was supported by a grant from the National Science Foundation, CHE-1800236. The computational work was supported by the Donors of the American Chemical Society Petroleum Research Fund. High performance computational resources were provided by the Louisiana Optical Network Infrastructure (<http://www.loni.org>) and by the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy under contract #DE-AC02-05CH11231.

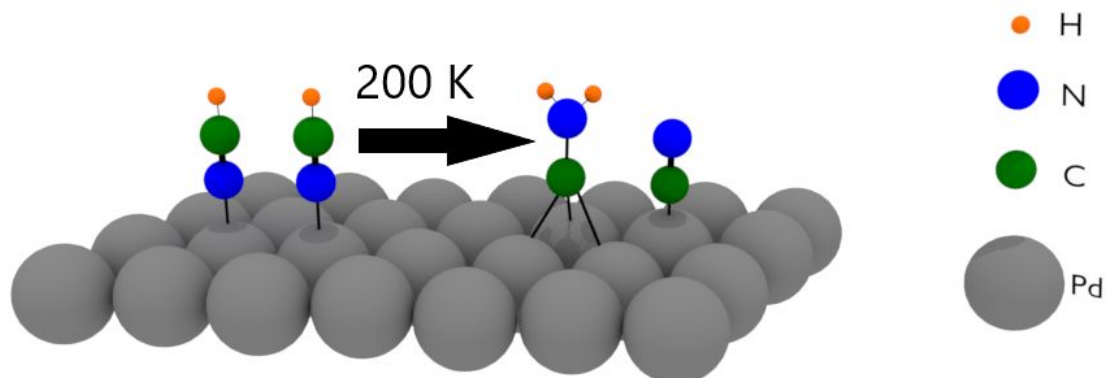
## References

- M. E. Kordesch, T. Lindner, J. Somers, W. Stenzel, H. Conrad, A. M. Bradshaw and G. P. Williams, *Spectrochim. Acta A*, 1987, **43**, 1561-1566.
- M. E. Kordesch, W. Stenzel and H. Conrad, *Surf. Sci.*, 1988, **205**, 100-116.
- D. Jentz, H. Celio, P. Mills and M. Trenary, *Surf. Sci.*, 1995, **341**, 1-8.
- D. Jentz, P. Mills, H. Celio, M. Belyansky and M. Trenary, *J. Chem. Phys.*, 1996, **105**, 3250-3257.
- D. Jentz, P. Mills, H. Celio and M. Trenary, *Surf. Sci.*, 1996, **368**, 354-360.
- H. Celio, P. Mills, D. Jentz, Y. I. Pae and M. Trenary, *Langmuir*, 1998, **14**, 1379-1383.
- X. Hu and M. Trenary, *J. Phys. Chem. C*, 2012, **116**, 4091-4096.
- X. Hu, J. Yin, R. J. Meyer and M. Trenary, *J. Phys. Chem. C*, 2015, **119**, 14506-14512.
- G. E. Hyde and D. F. Hornig, *J. Chem. Phys.*, 1952, **20**, 647-652.
- T. Nakagawa and Y. Morino, *Bull. Chem. Soc. Jap.*, 1969, **42**, 2212-2219.
- J. Pacansky and G. V. Calder, *J. Mol. Structure*, 1972, **14**, 363-383.
- R. B. Bohn and L. Andrews, *J. Phys. Chem.*, 1989, **93**, 3974-3979.
- B. Chatterjee, D. H. Kang, E. Herceg and M. Trenary, *J. Chem. Phys.*, 2003, **119**, 10930-10940.
- D. C. Ford, Y. Xu and M. Mavrikakis, *Surf. Sci.*, 2005, **587**, 159-174.
- J. Gómez-Díaz and N. López, *J. Phys. Chem. C*, 2011, **115**, 5667-5674.
- C. W. J. Bol, J. D. Kovacs, M. Chen and C. M. Friend, *J. Phys. Chem. B*, 1997, **101**, 6436-6442.
- A. Kis, R. Barthos and J. Kiss, *Phys. Chem. Chem. Phys.*, 2000, **2**, 4237-4241.
- X. Feng, M. K. Abdel-Rahman, C. M. Kruppe and M. Trenary, *Surf. Sci.*, 2017, **664**, 1-7.
- I. Waluyo, Y. Ren and M. Trenary, *J. Phys. Chem. Lett.*, 2013, **4**, 3779-3786.
- P. L. Hagans, I. Chorkendorff and J. T. Yates, *J. Phys. Chem.*, 1988, **92**, 471-476.
- G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.
- J. Klimes, D. R. Bowler and A. Michaelides, *J. Phys.: Condens. Matter*, 2010, **22**.
- J. Klimes, D. R. Bowler and A. Michaelides, *Phys. Rev. B*, 2011, **83**.
- B. Hammer, L. B. Hansen and J. K. Nørskov, *Phys. Rev. B*, 1999, **59**, 7413-7421.
- P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953-17979.
- G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758.
- M. Methfessel and A. T. Paxton, *Phys. Rev. B*, 1989, **40**, 3616-3621.
- N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Holt, Rinehart and Winston, New York, 1976.
- J. Neugebauer and M. Scheffler, *Phys. Rev. B*, 1992, **46**, 16067-16080.
- G. Henkelman, B. P. Uberuaga and H. Jonsson, *J. Chem. Phys.*, 2000, **113**, 9901-9904.
- G. Henkelman and H. Jonsson, *J. Chem. Phys.*, 1999, **111**, 7010-7022.
- S. R. Bahn and K. W. Jacobsen, *Comput. Sci. Eng.*, 2002, **4**, 56-66.

## ARTICLE

## Journal Name

- 33 R. E. Hoffman and D. F. Hornig, *J. Chem. Phys.*, 1949, **17**, 1163-1163.
- 34 H. B. Friedrich and P. F. Krause, *J. Chem. Phys.*, 1973, **59**, 4942-4948.
- 35 P. A. Gerakines, M. H. Moore and R. L. Hudson, *Icarus*, 2004, **170**, 202-213.
- 36 I. Couturier-Tamburelli, N. Pietri, V. Le Letty, T. Chiavassa and M. Gudipati, *Astrophys. J.*, 2018, **852**.
- 37 K. N. Choi and E. F. Barker, *Phys. Rev.*, 1932, **42**, 777-785.
- 38 K. Momma and F. Izumi, *Journal of Applied Crystallography*, 2008, **41**, 653-658.
- 39 J. A. Herron, S. Tonelli and M. Mavrikakis, *Surf. Sci.*, 2012, **606**, 1670-1679.
- 40 M. E. Kordesch, W. Stenzel and H. Conrad, *Surf. Sci.*, 1987, **186**, 601-623.
- 41 A. J. R. Hensley, K. Ghale, C. Rieg, T. Dang, E. Anderst, F. Studt, C. T. Campbell, J.-S. McEwen and Y. Xu, *J. Phys. Chem. C*, 2017, **121**, 4937-4945.
- 42 X. Guo, A. Hoffman and J. T. Yates, *J. Phys. Chem.*, 1989, **93**, 4253-4258.
- 43 J. Wellendorff, T. L. Silbaugh, D. Garcia-Pintos, J. K. Nørskov, T. Bligaard, F. Studt and C. T. Campbell, *Surf. Sci.*, 2015, **640**, 36-44.
- 44 J. T. Fermann and S. Auerbach, *J. Chem. Phys.*, 2000, **112**, 6787-6794.
- 45 G. E. Gdowski, T. E. Felter and R. H. Stulen, *Surf. Sci.*, 1987, **181**, L147-L155.
- 46 P. B. Rasmussen, P. M. Holmblad, H. Christoffersen, P. A. Taylor and I. Chorkendorff, *Surf. Sci.*, 1993, **287-288**, 79-83.
- 47 M. E. Kordesch, W. Stenzel and H. Conrad, *Surf. Sci.*, 1986, **175**, L687-L692.
- 48 P. Mills, D. Jentz and M. Trenary, *J. Am. Chem. Soc.*, 1997, **119**, 9002-9009.
- 49 J. S. Somers, M. E. Kordesch, R. Hemmen, T. Lindner, H. Conrad and A. M. Bradshaw, *Surf. Sci.*, 1988, **198**, 400-412.



Two HCN molecules, adsorbed at 85 K in an upright orientation, react to form the aminocarbyne species, CNH<sub>2</sub>, on Pd(111) when the surface is heated to 200 K.