# THE STRUCTURE AND BONDING OF K AND Na CYANIDE ON Pd(100): LEED AND VALENCE LEVEL SPECTROSCOPY

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Received 20 June 1988; accepted for publication 23 September 1988

The structure of the overlayer formed on Pd(100) from the reaction of K and CN at temperatures above 800 K has been determined with LEED. The KCN which forms a phase with a  $\sqrt{5} \times \sqrt{5}$  LEED structure has been identified with He\* spectra as a covalently bonded alkali cyanide with an ionic adsorbate-metal bond.

### 1. Introduction

In recent reviews, Heskett and Bonzel have described the current status of alkali metal-CO coadsorption on surfaces [1] with special regard to the range of the alkali-CO interaction. It has been concluded that the interaction is predominantly short ranged. Many different LEED patterns produced in the CO/K/Pt(111) system [2] which were related to clearly detectable shifts of the CO stretch frequency. While these shifts were interpreted in terms of a short range interaction, it is obvious that the existence of ordered overlayer structures must be due to a long range interaction. In this paper we present data for K-CN coadsorption on Pd(100) which may be compared with K-CO systems. In particular, the formation of a chemisorbed phase with a simple LEED pattern and with a well defined electronic structure allows a relative complete characterisation of the KCN/Pd(100) system.

Our investigations show that the KCN adsorbate system consists of two distinct phases: an ionic "salt" of KCN, identical to the bulk phase, and a chemisorbed form of KCN with a covalent K–CN bond. We have been able to verify that short range interactions between the CN and the K "promoter" (see ref. [1]) occur and that the constituent species are also close to each other in real space [3,4].

In earlier papers we have shown that adsorbed CN is produced by the dissociative adsorption of NCCN on Pd(100) [5] at 300 K and that HCN adsorbs dissociatively on this surface [6] also resulting in adsorbed CN. These two adsorbates have been studied with UV photoelectron spectroscopy using

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synchrotron radiation on Pd(111), where an assignment of the molecular orbitals of the chemisorbed CN species was achieved [7].

Penning ionisation electron spectroscopy (PIES) has been used in this study because the extreme surface sensitivity of the PIES technique allows us to detect alkali metals at very low coverage [8] and, since the Pd d-band is not present in the spectra, also makes it possible to detect spectral features at low binding energy which would otherwise be hidden by the Pd d-band emission [9]. The deexcitation of metastable rare gas atoms occurs in front of or at the surface by tunneling of an electron into the unoccupied core level of the metastable atom. PIE spectra therefore contain only information on the electronic structure of the outermost layer [9]. Contributions to UV spectra, however, are composed of both adsorbate and substrate features due to the escape depth of the emitted photoelectrons [10].

### 2. Experimental

The UHV systems for the measurements are described elsewhere [11]. The K was evaporated from a SAES Getters source, the NCCN from thermal decomposition of AgCN and the HCN by backfilling the chamber with HCN vapor from an ampoule containing liquid HCN. Temperatures were measured with NiCr–Ni thermocouples spot-welded to the sample, heating rates were typically 5 K/s.

### 3. Results and discussion

In fig. 1 a number of He\* PIES spectra of KCN layers heated to various temperatures are shown. In fig. 1a a K multilayer (~ 6 layers thick) was exposed to 6 L (1 L =  $1 \times 10^{-6}$  Torr  $\cdot$  s) of NCCN. The PIE spectra exhibit three strong peaks in the valence level region and no electron emission in the region where the Fermi energy  $E_F$  is expected. The valence features observed in PIE spectra of this phase have energetic spacings identical to those reported by Pulm et al. [12] in a photoemission study of crystalline NaCN(100). We therefore assign the three features in fig. 1a to the valence levels of CN<sup>-</sup>, which are the  $4\sigma$ ,  $1\pi$ , and  $5\sigma$  at 10.7, 8.7, 7.4 eV binding energy with respect to the Fermi level ( $E_F$ ), respectively [4]. The conclusion is that NCCN adsorbs dissociatively on K multilayers at 100 K, and forms bulk-like ionic KCN.

Substituting HCN for NCCN did not cause any change in the resulting spectra [13]. Upon exposing the K multilayer to HCN we found a significant increase of the  $H_2$  partial pressure in the chamber. Immediately after the start of HCN exposure, the  $H_2$  pressure rises, subsequently decreasing nearly exponentially to the value observed when the hot crystal is exposed to the



Fig. 1. Penning spectra of ~6 layers of potassium (K) exposed to 6 L C<sub>2</sub>N<sub>2</sub> at 110 K after stepwise annealing to (a) 300 K, (b) 490 K, (c) 690 K, (d) 840 K. The region near E<sub>F</sub> is magnified by a factor displayed in the figure. The peaks marked "A" are due to interatomic Auger transitions [3]. The shaded area in (c) and (d) shows the mixed level at about 1.5 eV.

same HCN pressure (this background pressure is produced by dissociation of gaseous HCN in the ionisation chamber of the mass spectrometer and corresponds to the HCN cracking pattern).

The observed increase of the  $H_2$  partial pressure shows that HCN also adsorbs dissociatively on the K multilayer, with the hydrogen liberated into the gas phase and CN reacting with the K atoms. This reaction ends after the depletion of the metallic K layer. Additional HCN physisorbs on top of the ionic KCN and is easily detected in UPS and PIES.

The PIE spectra measure only the outermost layer of the adsorbate/surface complex. The PIE spectrum did not change upon heating to 300 K although  $C_2N_2$  desorption was observed. He I UPS, however, showed an additional feature at 6.2 eV binding energy [4], which, on the basis of the greater escape

depth of photoemitted electrons, indicates the presence of a second phase below the ionic KCN. This was indeed found to be a case, as revealed by further heating of the composite layer.

Heating to 490 K caused a shift towards lower binding energy of the CN valence features, and the appearance of a K(4s) related peak at  $E_{\rm F}$  (fig. 1b). The K(4s) emission indicates the presence of excess metallic K released by the recombination of two CN groups to  $C_2N_2$  which desorbs. The energy shift of the valence levels is ascribed to a change of the Madelung energy due to the decrease in thickness of the "bulk" K<sup>+</sup>CN<sup>-</sup>.

Subsequent heating to 690 K induces strong changes in the valence features (fig. 1c), and new structures can be identified. After annealing to 840 K (fig. 1d) the He<sup>\*</sup> PIES features have been completely altered relative to the ionic phase and only a small contribution from metallic K is observed near  $E_{\rm F}$ . Ne<sup>\*</sup> PIES as well as UV spectra taken with 40 eV photons at the Berlin synchrotron BESSY [14] showed only two relatively narrow emissions features at 6.2 and 8.9 eV.

In contrast to these results the He\* spectrum (fig. 1d) exhibits a more complicated structure. The features marked A have been assigned to interatomic Auger transitions and will be discussed below. The peaks I and II correspond to the features observed in the UV spectra as is evident from the relative spacing; but they show an overall shift of  $\sim 1$  eV to higher binding energy if  $E_{\rm F}$  is identified with the emission onset of the K(4s) peak. The metastable He\* is a laterally resolving probe and can interact differently with metallic K and chemisorbed KCN. The difference of the interaction in turn leads to a difference of the effective excitation energy and shifts the peaks on the kinetic energy scale [9]. The Fermi level for the KCN species has to be identified with the upper edge of the hatched feature in fig. 1c and 1d. This peak (marked as III) - not observable in UV spectra - corresponds to a valence level of the chemisorbed KCN and has been assigned to the bonding combination of orbitals which are unoccupied in the separate K and CN constituents [4]. In table 1 we summarize the binding energies and orbital assignments of all observed structures.

The splitting of peak I is related to the singlet-to-triplet conversion of the He\* [15]. A thorough discussion of this process is beyond the scope of this paper and will be published separately [16].

In further measurements [3], it was found that He<sup>\*</sup> PIE spectra and the He I and Ne II UV spectra have additional electron emission structures at constant kinetic energy, while Ne<sup>\*</sup> and Ne I UV spectra do not. Measurements of the K(3p) core level of the KCN phase at 840 K determined that the 3p level lies at 17.3 eV binding energy (BE) and can be excited with He<sup>\*</sup>. It was concluded that interatomic Auger processes, involving a K(3p) core-hole which is filled by electrons from the three observed levels at 6.2, 8.9 and 1.5 eV binding energy, cause the additional features at constant kinetic energy [3]. In

	Pd(111)/CN <sup>h)</sup>	Pd(100)/K	Pd(100) KCN (840 K)	K <sup>+</sup> CN <sup>-</sup>
<u>CN (2π)</u>	-5 <sup>c)</sup>	- )	1.5 <sup>e)</sup>	_
K (4p)	-	$-0.8^{\text{ d}}$		-
K (4s)	_	0.4 )	6.2 <sup>e)</sup>	_
CN (5σ)	5.0	- )		7.4
$CN(1\pi a'')$	6.1		6.2	8.7
$CN(1\pi a')$	7.2	-	6.2	8.7
CN (4σ)	9.1	_	8.9	10.7

Orbital assignments [4] and binding energies (with respect to  $E_F$ )<sup>a)</sup> of the covalent K/CN Species on Pd(100)

<sup>a)</sup> The binding energies of unoccupied orbitals above  $E_{\rm F}$  have been taken negatively.

<sup>b)</sup> From ref. [7].

Table 1

<sup>c)</sup> From refs. [20,21].

<sup>d)</sup> From ref. [22].

e) K/CN mixed orbitals.

order to support the interpretation based on the variation of the excitation energy used, measurements with Na, where the core level lies beyond the range of excitation energies available from He\* PIES were carried out.

The comparison of He\* PIE spectra of K/CN and Na/CN prepared under identical conditions is shown in fig. 2. The valence features are identical, but a difference spectrum clearly shows the A features indicated in fig. 1. The contribution due to the interatomic Auger effect in the K/CN system is thus conclusively demonstrated. As expected, the binding energy of the Na(2p) core



Fig. 2. Penning spectra of K and Na layers corresponding to the minimum of the work function after saturation with CN (10 L NCCN) at 400 K and annealing to 690 K.



Fig. 3. LEED pattern of the  $(\sqrt{5} \times \sqrt{5})$ R26°34′ structure, showing the primitive lattice cells of the two symmetry domains. The lower picture shows the suggested real space lattice.

level (31 eV [17]) is too large for the creation of a hole with He<sup>\*</sup>. Additionally we demonstrate that the replacement of K by Na causes only negligible changes in the electronic structure of the surface molecule. The assignments of table 1 also apply to chemisorbed NaCN with the Na orbitals correspondingly adapted. The KCN species of fig. 1d can be produced by thermal decomposition of multilayer  $K^+CN^-$ . Preadsorption of a K layer corresponding to the work function minimum followed by NCCN adsorption at 400 K leads to spectra identical to that of fig. 1d. Interchanging the adsorption sequence at 400 K also results in the same species.

HREELS measurements of this phase show that only one species of KCN is present, with a CN stretching frequency of 232 meV and a KCN-substrate mode at 17 meV [4]. On the basis of the combined measurements of this system, we conclude that a linear form of KC  $\equiv$  N is adsorbed. The formation of a surface molecule with a well defined stoichiometry must be due to short range interaction between K and CN. The effect of additional long range interactions leads to an ordering of the chemisorption layer. While the ionic multilayer phase is disordered, a sharp ( $\sqrt{5} \times \sqrt{5}$ )R26°34′ LEED pattern has been observed on Pd(100) for the phase corresponding to fig. 1d, which is shown schematically in fig. 3a, along with the real space lattice (fig. 3b). In fig. 3a the two possible symmetry domains of the primitive cell are indicated. The real space lattice corresponds to a KCN coverage of  $\theta_{\rm KCN} = 0.2$  and is based on the finding that saturating a K precoverage near or below the work function minimum ( $\theta_{\rm K} = 0.25$  [18]) with CN minimized the signal of metallic K in the Penning spectra.

Three high symmetry adsorption sites are possible on a (100) surface: on top, bridged and four-fold hollow. The bridge site is improbable. A shift of the adsorbate net to bridge K/CN adsorbate sites would leave empty bridge sites in the center between four KCN units which are equivalent to the occupied sites. Increasing the K and CN doses should fill them and – after saturation – lead to a centered  $\sqrt{5} \times \sqrt{5}$  LEED pattern, which was never observed. Metallic alkali atoms are assumed to be adsorbed on transition metals in the four-fold hollow sites of the (100) surface [19]. Since the coexistence of KCN and K is documented in the Penning spectra, we suggest that the KCN molecules are located on top of the Pd atoms such that the four-fold sites can simultaneously be occupied by K.

From an inspection of table 1 it is clear that more than 8 valence electrons are necessary to fill the orbitals resulting from the KCN bond. We conclude that the KCN bond is indeed mostly covalent, but that the whole KCN molecule has a net negative charge. This implies that the chemisorption bond between the metal and  $(\text{KCN})^{\delta^-}$  is predominantly due to the image charge interaction. The thermal stability of the chemisorbed KCN supports this conclusion.

The essential difference between CO and CN coadsorbed with K atoms is the formation of the KCN molecule which can be considered as a new species forming a single ordered structure. For CO interacting with K the coordination with different numbers of K atoms determines the resulting layer without essential changes in the molecular orbitals.

### 4. Summary

The ordered overlayer formed from the reaction of K and CN at temperatures above 800 K have been determined for Pd(100) with LEED. The  $\sqrt{5} \times \sqrt{5}$  pattern observed for this phase has been interpreted with the help of valence level spectra.

Penning and UV spectra indicate that the lower temperature phases formed upon K/CN coadsorption are composed of ionic K cyanide, with a distinct interface layer between metal surface and bulk K/CN. The chemisorbed alkali-cyanide layer which remains after heating to 840 K has a covalent intramolecular bond. Analysis of the valence spectra and orbital structure suggests that a net negative charge remains on each adsorbed unit, resulting in a stable adsorbate-metal bond.

### Acknowledgement

This work was funded by the Deutsche Forschungsgemeinschaft under Sonderforschungsbereich 6.

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