# CYANOGEN ADSORPTION ON Pd(110) AT LOW TEMPERATURES: A STUDY WITH ANGLE-RESOLVED PHOTOEMISSION, LEED AND THERMAL DESORPTION

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The adsorption of cyanogen,  $C_2N_2$ , on Pd(110) has been studied as a function of temperature using thermal desorption spectroscopy (TDS), angle-resolved ultraviolet photoelectron spectroscopy (ARUPS), LEED and work function measurements. At temperatures below 100 K multilayers are formed; flashing of these to successively higher temperatures gives several different states of the surface. At 200 K a state which shows a  $c(2 \times 2)$  LEED pattern and which is assigned as a monolayer of parallel-bonded  $C_2N_2$  molecules is obtained. The molecules are predominantly aligned perpendicular to the close-packed rows of Pd atoms, i.e. along [001]. Six valence orbital ionisations are observed and assigned; these assignments indicate strong  $\pi$  interactions with the surface. Above 200 K dissociation to CN occurs. Desorption between 100 and 200 K is complex; there is some evidence which suggests a tilted molecular species here.

# 1. Introduction

Studies of cyanogen interaction with clean single crystal metal surfaces were first presented some 14 years ago [1]. Since then there have been a number of other studies, and in the last two years there has been a substantial increase in the number of publications [2-25], many of which have been concerned with the surface dissociation reaction to form CN. CN is of interest for several reasons, but particularly because of the comparison of coordination mode with that of CO, and our interest is partly motivated by this question, which will be discussed in a subsequent paper.

0039-6028/89/\$03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) Less attention has been paid to the coordination mode of  $C_2N_2$  itself, and little information has been available on this question until the recent work of the Berlin group [18–24], who have presented convincing evidence that  $C_2N_2$ can be adsorbed with a  $\pi$  bonded parallel geometry on Pd(100) and Pd(111). With commendable prescience, the most recent work from this group [24] has suggested that angle-resolved photoemission studies should be carried out on a (110) surface. We present the results of such a study here, and show that the azimuthal orientation, and complete molecular orbital assignments, can be deduced.

## 2. Experimental

Experiments were carried out in two VG ADES instruments equipped with facilities for LEED, TDS, EELS, and ARUPS; one of the ARUPS systems was attached to the TGM2 monochromator at the synchrotron radiation laboratory BESSY in Berlin. The same Pd(110) crystal, mounted on an azimuthally adjustable manipulator with liquid nitrogen cooling, was used for all experiments. At the synchrotron the total-energy resolution (monochromator and analyser) was set to  $\sim 200$  meV.

Cyanogen was generated by thermal decomposition of a sample of silver cyanide (Riedel-de Haen) in a tube attached to the inlet manifold [1]. Dosing was carried out with a pin-hole effusion source  $\sim 0.5$  cm from the crystal [26], or for room temperature work, from the system ambient. Dosing was reproducible with this source, but it is not calibrated; we give the doses in arbitrary units.

Thermal desorption spectra were obtained at a heating rate of 2.5 K s<sup>-1</sup>. ARUPS experiments were carried out in the crystal azimuth planes which include the [110] and [100] crystal surface directions; azimuth orientation to within  $\pm 2^{\circ}$  was possible using the LEED optics. The cleaning procedures were the same as in previous studies using this crystal [27], but after cooling a final flash to 500°C was carried out to remove traces of CO and H. The normal emission ARUPS spectrum, including the scattered tail, and the work function measured from the UPS, were fully reproducible with this procedure; well ordered (1×1) LEED patterns were obtained and no impurities were detectable by Auger spectroscopy.

 $\Delta\phi$  measurements were made using the secondary electron cut-off of the UPS. A standard bias potential of -5.0 eV was applied to the crystal with the analyser set for normal emission, and the computer control was set to scan the emission onset region. As a check the Fermi level was also scanned; this was invariant. The work function was determined by subtracting the difference between the inflection points of the two edges from the photon energy. For clean Pd(110) a value of 5.10 eV was obtained; we estimate the absolute error

to be about 0.1 eV, but relative values are reproducible to better than  $\pm 25$  meV.

## 3. Results and discussion

#### 3.1. Thermal evolution of multilayer and assignment of the monolayer condition

He I ARUPS at normal emission coupled with TDS have been used to follow the evolution of the surface with exposure to  $C_2N_2$  at 90 K, and with subsequent heating. Fig. 1 shows the ARUPS as a function of temperature following a large exposure; changes with increasing coverage mirror the heating changes up to 200 K, at least approximately. In outline, fig. 1 shows



Fig. 1. He I ARUPS at normal emission for Pd(110) dosed with 200 units (see text) of  $C_2N_2$  at 80 K, flashed to the temperatures indicated and cooled to about 100 K before running each spectrum. Photon incidence angle  $\alpha = 60^{\circ}$  in the [001] azimuth of the crystal surface.



Fig. 2. Thermal desorption traces for amu = 52 ( $C_2N_2$ ) from Pd(110) exposed to increasing doses of  $C_2N_2$  at 80 K. Doser units: (a) 40, (b) 60, (d) 80, (d) 160, (e) 240.

an evolution from a 3-peak system to a 2-peak system, and finally to a 1-peak system.

Some clarification of these changes in UPS is provided by the TDS of fig. 2.  $C_2N_2$  is evolved in two main temperature regions, in agreement with earlier studies on other surfaces [1-3, 6-18]. The lower temperature region close to room temperature is usually labelled  $\alpha$  and the higher temperature region  $\beta$ , and on some surfaces  $\beta_1$  and  $\beta_2$  peaks are clearly resolved; here there is a shape change in the  $\beta$  region for low coverages which suggests that  $\beta_1$  is at 760 K and  $\beta_2$  is at 840 K. The  $\alpha$  region is usually assigned to molecular desorption and  $\beta$  to reactive desorption, probably from recombination of CN groups on the surface. However, the assignment of the  $\alpha$  peak to molecular desorption has been queried, and on Pd(100) there is evidence for decomposition to CN below the temperature at which the  $\alpha$  peak desorbs [18]. At high

exposures a very sharp peak appears at about 120 K which we associate with multilayer desorption [18]. In addition to the multilayer peak the region below 300 K shows considerable complexity. Variation of the heating rate confirmed that this complexity is indeed a physical property of the adsorbate layer and not an artefact of the experimental procedure.

The double-peak structure of fig. 2a, with a main peak at 230 K and subsidiary one at 275 K, can be obtained over a range of exposures, with varying intensity, and we correlate this double peak  $\alpha$  with desorption from the first layer of adsorbed C<sub>2</sub>N<sub>2</sub> and the change from fig. 2a to fig. 2b with saturation of this first state. The 275 K component is clear at all exposures, but the 230 K peak is overlaid by other structures at high exposures. At very low coverages there are indications that only the high temperature component persists, but we have not investigated this further.

At higher coverages (figs. 2b-2e) several structures appear on the low temperature side of the 230 K peak. The obvious interpretation is that we are observing desorption from the second layer, and possibly others, resolved from the multilayer desorption, but an alternative interpretation will be considered later. The exposure used to produce the spectra of fig. 1, 200 units, is intermediate between those of figs. 2d and 2e, so the 80 K 3-peak spectrum of fig. 1 clearly corresponds to emission from a multilayer. Larger exposures than this cause broadening in the UPS spectra, shifts to higher binding energies, and ultimately multiple peaks; we believe these are effects of charging. From the thermal desorption measurements, it is necessary to heat a multilayer system to 170-200 K to produce a state equivalent to the 2-component  $\alpha$ -TDS peak, approximately monolayer. This corresponds to a 2-peak UPS, but between 170 and 200 K the intensity of the 6.3 eV UPS peak is still changing rapidly and the peak positions are shifting. Further information comes from the work function measurements shown in fig. 3a. As the multilayer is heated there is an initial discontinuity, possibly from charging, and then a rise to a maximum  $\Delta \phi$  of +1.6 eV at 200 K followed by very steep drop through the  $\alpha$ -TDS structure.

As heating is extended beyond 200 K there are further substantial changes in the appearance of the UPS which correlate with the  $\alpha$ -TDS and with the steep drop in  $\Delta\phi$ . The apparent single peak UPS for the 270 K condition stays constant over the plateau region of  $\Delta\phi$  (+0.95 V) but the peak is reduced slightly in intensity by heating to 700 K. This correlates with a decrease in the work function. The single strong peak in normal emission UPS is characteristic of CN on metal surfaces [4,5,16,18,25], and it disappears over the region of the  $\beta$  peak in the TDS. The same UPS and  $\Delta\phi$  values can be obtained by saturating a clean Pd(110) surface at room temperature: the  $\Delta\phi$  experimental results are indicated in fig. 3b. The detailed analysis of the results at room temperature and higher will be presented separately [28]; for the moment we note that the indications from both UPS and  $\Delta\phi$  measurements are that the



Fig. 3. (a) Work function of a Pd(110) surface which has been dosed with 200 units of  $C_2N_2$  at 80 K and then heated to successively higher temperatures. (b) Work function of a clean Pd(110) surface at 300 K exposed to successively larger amounts of  $C_2N_2$  from the system ambient: exposures are uncorrected for ion gauge sensitivity.

dissociation of  $C_2N_2$  takes place mainly over the range 230-270 K. We correlate the rise in  $\Delta\phi$  up to 200 K with the removal of outer layers, and the drop above 200 K with the dissociation to give surface CN as the  $\alpha$  desorption occurs. The maximum excursion in  $\Delta\phi$  at 200 K thus represents the best approximation we can obtain to monolayer  $C_2N_2$  coverage. However, since no plateau in the  $\Delta\phi$  curve is obtained at 200 K it is likely that small amounts of CN are present in the  $C_2N_2$  monolayer. Any interference in the spectra from CN will be much less than that produced by "second layer" effects at lower flashing temperatures.

LEED studies have also been carried out as a function of temperature. As expected, the multilayer gives diffuse scattering superimposed on a  $(1 \times 1)$ pattern. The multilayer was found to be very susceptible to electron beam damage, so subsequent experiments were carried out by moving the crystal slightly for each observation. At 150 K a weak  $c(2 \times 2)$  pattern appears and persists as the temperature is raised. A  $c(2 \times 2)$  pattern is still observed through the region of the steep fall in  $\Delta \phi$ ; at higher temperatures other patterns evolve which will be discussed with the UPS data. After room temperature adsorption of  $C_2N_2$  a  $c(2 \times 2)$  pattern is also observed, which is due to adsorbed CN. While it might be argued that the  $c(2 \times 2)$  pattern in the region of 200 K is due to small amounts of  $C_2N_2$  dissociation, we do not observe any intensity increase in the pattern between 200 and 300 K, so we believe that both  $C_2N_2$  and CN form  $c(2 \times 2)$  structures on the surface. The 200 K state of the surface, which we believe to be principally monolayer  $C_2N_2$ , has been further characterised by ARUPS using synchrotron radiation.

# 3.2. ARUPS of the $C_2N_2$ monolayer

Studies of the angular variation of the photoemission have been made using unpolarised HeI radiation and synchrotron radiation. Similar results are obtained in both studies, but much better defined effects are observed in the synchrotron work, and only these will be reported here.

Fig. 4 shows a set of spectra from the monolayer as a function of  $\theta$ , the electron exit angle in the [001] azimuth plane from the surface normal. The diagram also shows the spectrum of the multilayer from which the monolayer was prepared, together with the relative positions of the gas-phase ionisations [29]. A total of five individual features A-E can be picked out; their ionisation energies and assignments are summarised in table 1. B at 5.6 eV binding energy is the most prominent at all angles and shifts slightly to higher energy as  $\theta$  increases. D is seen most readily at high angles, but mainly because of a reduction of intensity C. A is evident at high angles but has little intensity at normal emission. The multilayer spectrum can be readily correlated with the gas-phase spectrum on the assumption that  $5\sigma_g$  and  $4\sigma_u$  are not resolved. In the gas phase  $4\sigma_u$  is noticeably weaker than  $5\sigma_g$ , and this probably accounts for the slight upward shift of the central component of the multilayer spectrum.

The monolayer spectrum is clearly different from the gas phase and multilayer spectrum, both in intensity distribution and in the number of bands. An adsorption model in which the  $C_2N_2$  axis is perpendicular to the surface is immediately ruled out since there are more than four components, and in  $C_{\infty\nu}$  symmetry the degeneracies of the  $\pi$  orbitals are maintained. An inclined or parallel geometry, or a non-linear molecule, will not have these degeneracies and a total of six ionisations is expected.

Further information comes from variation of azimuth and of photon energy. Intensity changes are observed, but all bands except for B are invariant in energy. Figs. 5 and 6 show that B shifts by up to 0.4 eV according to the experimental conditions, so we consider that B has two components, as might be suspected from the high intensity and the shift with  $\theta$ . We therefore have evidence for a total of six ionisations, measured energies are shown in table 1. The intensity shifts with azimuth are strong indications that the chemisorbed molecule has a preferred azimuth orientation; (110) surfaces are particularly good for producing such orientations, particularly for species which themselves are strongly directional [30]. However, the effects which we observe are not very strong, so the ordering is probably only partial.



Fig. 4. ARUPS from a multilayer of  $C_2N_2$  (200 units at 80 K) and from a monolayer formed by flashing this to 200 K. The relative positions of the molecular gas-phase ionisations are shown, together with a proposed correlation which is discussed in detail in the text.

Table 1									
Ionisation	energies 1	below the	Fermi	level,	for	monolayer	$C_2N_2$ o	n Pć	<b>i</b> (110)

Band	Energy (eV)	Assignment <sup>a)</sup>	
	4.9	$\pi_{g}(a_{2})$	
В	5.4	$\sigma_a(a_1)$	
	5.9	$\pi_{g}$ (b <sub>1</sub> )	
С	6.7	$\sigma_{\rm u}$ (b <sub>1</sub> )	
D	8.0	$\pi_{\mu}$ (b <sub>2</sub> )	
E	9.0	$\pi_{u}(a_{1})$	

<sup>a)</sup> Assignments, discussed in the text indicate the parent orbitals of the free molecule and relate these to  $C_{2\nu}$  geometry for a parallel adsorbed molecule.



Fig. 5. Normal emission of a 200 K monolayer of  $C_2N_2$  as a function of photon incidence angle in the two principal azimuths.

The highest point group symmetry possible for a parallel bonded molecule is  $C_{2v}$ ; this also allows some bending of the molecule perpendicular to the surface. Lower symmetries will also give six components but with fewer distinguishable representations;  $C_{2v}$  symmetry is a convenient assumption for labelling purposes and we show below that the major features are consistent with this being the correct description. In  $C_{2v}$  the HOMO of  $C_2N_2$ ,  $\pi_g$ ,  $C \equiv N$ bonding but antisymmetric with respect to  $\sigma$  and therefore weakly C–C antibonding, splits into  $a_2$ , distributed parallel to the surface with two node planes perpendicular to the surface, and  $b_1$  distributed perpendicular to the surface and therefore with only one node plane perpendicular to the surface.

Similarly  $\pi_u$  splits into  $b_2$  parallel to the surface with one node plane, and  $a_1$  perpendicular to the surface with no node planes. In a parallel geometry



Fig. 6. Mirror plane experiments on a 200 K monolayer of  $C_2N_2$ . In the upper half the analyser is set off-normal in the [001] azimuth plane and the electric vector of the s-polarised light is set either parallel or perpendicular to the observation plane. The lower half shows the same experiment in the [110] azimuth.

 $5\sigma_{g}$  (a<sub>1</sub>) and  $4\sigma_{u}$  (b<sub>1</sub>) are unlikely to interact strongly with the surface, and the same is true of  $\pi_{g}$  (a<sub>2</sub>) and  $\pi_{u}$  (b<sub>2</sub>). These four are therefore likely to preserve their relative ordering in the transformation from free molecule to adsorbate. Mixing between the two b<sub>2</sub> orbitals, or the two a<sub>1</sub> orbitals, is likely to be very small because of the very different spatial orientation, unless substantial bending of the molecule occurs. In contrast  $\pi_{g}$  (b<sub>1</sub>) and  $\pi_{u}$  (a<sub>1</sub>) will interact strongly with the surface; a covalent interaction will stabilise both of these orbitals with respect to the other four. It is clear from fig. 4 that a correlation which follows this pattern can be drawn, though the a<sub>2</sub>-b<sub>2</sub> spacing is larger than expected (see below).

Fig. 5 shows the effect of changing photon incidence angle  $\alpha$  in the two principal azimuths, for normal emission. In addition to the shift of B already referred to, it is clear that there is a substantial increase in intensity of B with increasing  $\alpha$ , or increasing electric vector component perpendicular to the surface. This confirms the presence of an  $a_1$  component in B, as expected from the correlation suggested.

Fig. 6 shows the result of a mirror plane experiment, in which the analyser is set within one of the mirror planes of the surface, and the electric vector of the s-polarized light is set parallel or perpendicular to this plane; sometimes these geometries are called even and odd. In the [001] azimuth there is a general reduction in intensity in the out-of-plane geometry, but no shift of B. In contrast in the  $[1\overline{1}0]$  azimuth there is less intensity loss and a very pronounced shift of B. Bands which are due to ionisation of orbitals which are symmetric, or even, with respect to the observation plane will be reduced in intensity in the out-of-plane geometry; for perfect azimuthal ordering the bands should have zero intensity. Since in the  $[1\overline{1}0]$  azimuth the higher binding energy component of B increases in intensity in the odd geometry, this component must be odd, and the lower binding energy component must be even. Firstly, this confirms the contention above that B has both  $a_1$  and  $b_1$ components, and that  $b_1$  has the higher binding energy. Secondly,  $b_1$  can only be odd with respect to the  $[1\overline{10}]$  azimuth if the molecular axis lies perpendicular to this plane, since  $b_1$  is antisymmetric with respect to the plane perpendicular to the C-C axis. The molecules are therefore lying predominantly across the close-packed ridges of Pd atoms on the (110) surface. The lack of a shift of B, and the substantial intensity loss, in the [001] azimuth out-of-plane geometry, are due to the two components of band B, and band C, all being symmetric with respect to the experimental plane.

We have already noted that the angular ordering is not complete. Angular disorder might arise parallel or perpendicular to the surface, the latter giving some molecules inclined to the surface as has been proposed for cyanogen adsorption on Pd(100) [18,20]. Useful evidence can be obtained from the behaviour of band A, assigned as  $\pi_g$  (a<sub>2</sub>). On a perfectly ordered surface, with all molecules aligned perpendicular to the surface ridges, (a<sub>2</sub>) ionisation should be unobservable in all geometries so far discussed except for the out-of-plane experiments of fig. 6. Here  $a_2$  should be strongly enhanced, since this is the only geometry in which there is an electric vector component oriented appropriately. It is clear that A is observable readily in both geometries in fig. 6, this demonstrates again that the ordering is only partial. The lack of the expected symmetry effect is presumably due to a generally higher intensity of bands in the parallel geometries. However for normal emission band A is weak, as can be seen on fig. 4 and by a comparison of figs. 5 and 6. No normal emission from an a<sub>2</sub> ionisation is expected for any orientation parallel to the surface since the orbital node planes intersect along the normal.

However, tilted molecules would give emission from  $a_2$  along the surface normal. We therefore believe that the 200 K state of  $C_2N_2$  corresponds to molecules which are nearly all oriented parallel to the surface, but with only partial ordering along the [001] surface direction.

Inspection of fig. 1 shows that a shoulder in the same position as A is readily observable at normal emission at temperatures around 150 K, though not for the multilayer condition. Those temperatures correspond to the complex region of the TDS which might be due to second layer desorption. However, the substantial splittings of the  $\pi$  levels which are characteristic of the 200 K state are unlikely to persist in the second layer. An alternative interpretation of the complex TDS is that we are observing desorption from a compressed and tilted monolayer: the appearance of A at normal emission would then be understandable because of the lower symmetry of the adsorbate-surface complex. The other characteristic of the 140–170 K state is a high intensity UPS band in approximately the C position (6.7 eV). A similar spectrum has been reported for saturation coverage of C<sub>2</sub>N<sub>2</sub> on Pd(100) at 200 K, at which temperature there is evidence from PIES [18] and HREELS [20] that some of the C<sub>2</sub>N<sub>2</sub> molecules are tilted for this system.

We have measured HeI and HeII UPS spectra as a function of  $\theta$  and azimuth for a monolayer flashed to 150 K. The spectra show some features very similar to the 200 K spectra, particularly in the D/E region. In addition, both peaks B and C show appreciable shifts with energy and azimuth. We are probably observing a mixture of the parallel state with another, and the observation of the  $c(2 \times 2)$  LEED pattern at 150 K supports this. A detailed analysis is not practicable, but it seems likely that this second crowded state shows orbital splitting and azimuthal orientation. A tilted species fits these observations better than a physisorbed second layer. However, as pointed out in ref. [18], the bulk packing of solid  $C_2N_2$  is such that a second layer is likely to be inclined with respect to the first. A firm decision between some tilted molecules in the first layer, and tilted molecules in the second layer is difficult.

The general behaviour of  $C_2N_2$  on Pd(110) is fairly similar to that on Pd(100) [18] but the system is complicated by the slightly higher thermodynamic binding energy of CN on Pd(110), indicated by a  $\beta_1$ -TDS temperature of about 760 K compared to 540 K on Pd(100) [18]. Correspondingly the decomposition of  $C_2N_2$  on Pd(110) begins at a slightly lower temperature, 200 K, compared to about 230 K on Pd(100). It is therefore difficult to prepare fully ordered  $C_2N_2$  layers without some accompanying decomposition, and at lower temperatures the system is complicated by the more crowded state.

Many models for the ideal parallel aligned system are possible, but an attractive one which fits the  $c(2 \times 2)$  LEED and the orientation along [001] is shown in fig. 7. We note that a  $c(2 \times 2)$  surface corresponds to a full coverage: the Pd-Pd distance matches the N-N distance rather well. We have no information on the true registry with the surface, but the one shown is



Fig. 7. (a) Possible structure for the  $c(2 \times 2)$  monolayer of  $C_2 N_2$  formed at 200 K on Pd(110). Reasons for the particular registry with the substrate are discussed in the text. Distances are given in Å (1 Å =  $10^{-10}$  m), and the dimensions of  $C_2 N_2$  are given by the wave function contours calculated in ref. [32]. (b) Correlation of the gas-phase ionisations of  $C_2 N_2$  with those on the surface. The two sets have been aligned using the average of the two ionisations from the  $\sigma$ orbitals.

intuitively reasonable since it places the CN groups symmetrically with respect to the rows of Pd atoms, in positions where each molecule can maximise its interaction with surface atoms via the  $\pi$  orbitals. An alternative in which the C-C bond is above the rows is very unlikely in the light of the large splittings which we have observed for the  $\pi$  orbitals. HREELS studies of C<sub>2</sub>N<sub>2</sub> on Pd(111) show that the C-C stretching frequency is essentially unchanged from that in the free molecule. The conventional long-bridge coordination on top of pairs of atoms on adjacent rows is another possibility, but we favour the geometry shown because of the nature of the  $\pi$  orbital interactions. The right-hand half of fig. 7 shows a correlation of ionisation energies, re-drawn from figs. 3 and 5, in which we have aligned the two sets of levels using the baricentre of the two  $\sigma$  levels. Such a procedure is rather arbitrary; there is clearly some effect of coordination on these levels since their spacing is increased. However it is clear that not only are  $\pi_u$  (a<sub>1</sub>) and  $\pi_g$  (b<sub>1</sub>) stabilised, as expected on the basis of the simple arguments given above, but also  $\pi_{\rm u}$  (b<sub>2</sub>) is stabilised. While the actual alignment chosen is open to question, the  $\pi_{\rm u}(b_2) - \pi_{\rm e}(a_2)$  separation is appreciably greater than that in the molecule. Since in the "4-fold long bridge" site the  $C_2N_2$  will sit lower on the surface, interaction of  $\pi_u$  (b<sub>2</sub>) is increased. The arguments presented here have followed the traditional "stabilisation via covalent bonding to the surface" approach which has been widely used. High quality calculations on CO adsorption suggest that the covalent bond contribution may actually contribute only a very small part of the total orbital ionisation shift [31]. However, the arguments which we have presented only require that the orbitals which shift are in close proximity to the surface and do not depend on the mechanism of the shift. We note that the large work function increase is the opposite of that expected for substantial molecule-metal donation. Theoretical analysis of this system would be very valuable.

Finally, we note some minor inconsistencies in the interpretation presented. One is that the overlap of the contours of  $C_2N_2$  as shown in fig. 7a suggests some repulsion. The contours shown come from good quality MO calculations which have been shown to give good representations of crystal packing in the solid [32]. Another is that the discussion above in terms of  $C_{2v}$  symmetry suggests effects which have not been detected; in particular mirror plane variations are not observed for the  $b_2$  ionisation. This suggests that although  $C_{2v}$  symmetry is a reasonable approximate description, the true symmetry is lower, and the [001] azimuth plane of the surface is not a mirror plane of the adsorbate complex. Interpretation of these observations can only be speculative, but some bending of the molecules is a possible, and this could provide a rationalisation of the apparent interaction between  $5\sigma_g$  and  $4\sigma_u$  of fig. 7b. We believe that this system is worthy of further investigation, for example with HREELS.

# 4. Conclusions

We have evidence to support a parallel coordination of  $C_2N_2$  on Pd(110), in which the molecules are preferentially aligned perpendicular to the ridges of the surface, i.e. along [001]. This occurs on flashing multilayers to 200 K. At higher temperatures dissociation occurs, and at lower temperatures there is evidence for an additional adsorption mode, possibly tilted, above the multilayer desorption temperature. The parallel-coordinated molecules interact with the surface principally via the  $\pi$  orbitals.

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## Note added in proof

After this paper had been accepted, we were informed by Professor N. Rösch, Technische Universität München, Garching, Fed. Rep. of Germany, that LCGTO X $\alpha$  chemisorption model cluster calculations have been carried out on this system [33]. The results are in excellent agreement with the above deductions.

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