

# Photoemission from Ordered Physisorbed Molecular Phases N<sub>2</sub>/Graphite, N<sub>2</sub> and CO/Ag(111)

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Using angle resolved ultraviolet photoelectron spectroscopy (ARUPS) the two dimensional energy dispersions of ordered physisorbed monolayers of N<sub>2</sub> and CO/Ag(111) has been measured. For N<sub>2</sub>/graphite the ordered herringbone structure can be identified by correlating

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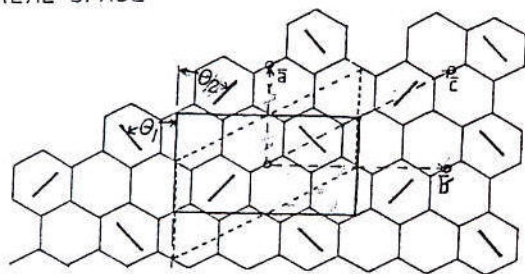
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the ARUPS data to recent LEED studies. For all systems investigated we observe a  $k$  dependent splitting of the  $5\sigma$  ( $3\sigma_g$ ) level which is a consequence of the intermolecular interaction of two molecules in the unit cell. The splitting is largest in the center of the Brillouin zone of the overlayer and disappears towards its zone boundary. The observed dispersion can be understood by a simple tightbinding calculation and is in good agreement with an *ab initio* bandstructure calculation.

### Introduction

The physical properties of physisorbed diatomic molecules have been studied to derive complete phase diagrams [1]. High surface area substrates like grafoil are necessary to employ specific heat measurements [2] or to perform neutron scattering (NSS) experiments [3]. More recently, it has been possible to observe LEED patterns of ordered layers of physisorbed N<sub>2</sub> and CO using highly oriented polycrystalline graphite (HOPG) as a substrate that provides large crystalline areas of graphite [4, 5]. The results indicate various commensurate and incommensurate phases at coverages close to the complete monolayer. Among them a herringbone structure is identified in which the molecules are oriented in plane (parallel to the surface) the molecular axes arranged almost perpendicular to each other. Physically, the symmetry of these arrangements mean, that two molecules are in the Surface Brillouin Zone (SBZ). In Fig. 1 schematic presentations of that herringbone structure for the real and the reciprocal space are given.

#### REAL SPACE



#### RECIPROCAL SPACE

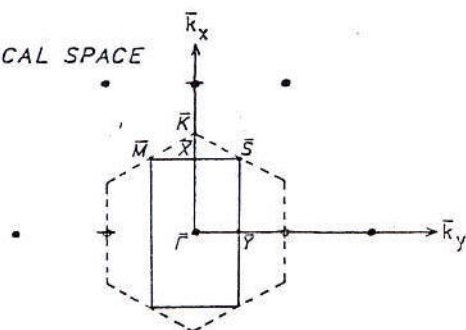


Fig. 1

Arrangement of physisorbed molecules in a  $\sqrt{3} (2 \times 1)$  superstructure when adsorbed on a hexagonal substrate. In real space the unit cell contains 2 molecules, as indicated. In reciprocal space the SBZ for the  $\sqrt{3}$  with the symmetry points at  $\bar{M}$  and  $\bar{K}$  are shown for comparison (dashed hexagon)

metry lines. Comparing to the 2D band structures of chemisorption systems like Chalcogen/Ni or CO/Ni [6] the dispersion is very similar although the adsorbate-surface interaction is quite different.

From this point of view the ARUPS investigations of physisorbed ordered systems are interesting as in these systems the heat of adsorption is even lower. On the other hand the existence of detailed LEED studies helps to support the ARUPS results and allows a very interesting combination of low temperature physics and surface science spectroscopies.

### Experimental and Results

The experimental details of our ARUPS measurements are published in detail elsewhere [8], for low temperature adsorption techniques see Ref. [9].

Our results for the systems N<sub>2</sub>/C, N<sub>2</sub>, CO/Ag(111) show similarities in various respects. Fig. 2 summarizes the spectra taken at normal emission for the three systems at about one complete monolayer (1 ML), respectively. Clearly the mol-

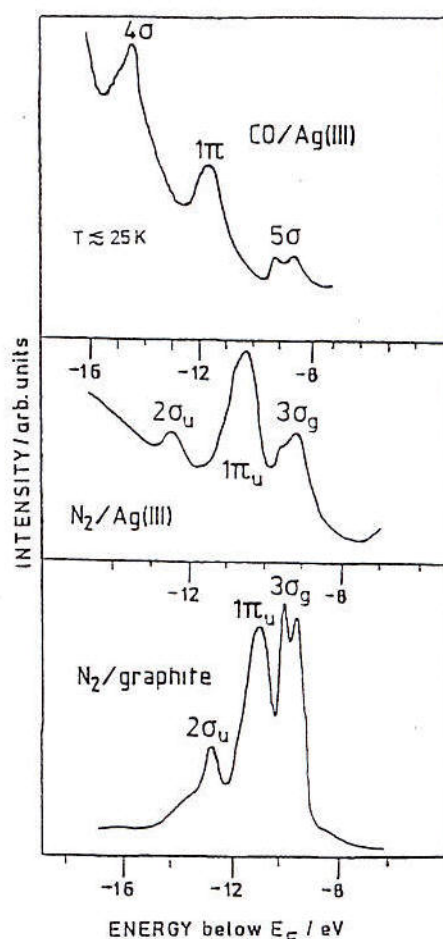


Fig. 2

Angle resolved photoelectron spectra taken at normal emission for CO/Ag(111) ( $h\nu = 19$  eV), N<sub>2</sub>/Ag(111) ( $h\nu = 21$  eV), and N<sub>2</sub>/graphite ( $h\nu = 25$  eV) at sample temperatures around 25 K

Angle resolved ultraviolet photoelectron spectroscopy (ARUPS) has been used in particular to study the electronic and geometric structure of chemisorbed atoms and molecules [6]. More recently, the method has been extended for physisorbed noble gas atoms [7], too. The observed topmost p-levels showed dispersion up to 0.6 eV along the main sym-



ecules are physisorbed, as their molecular ion state energy separation is nearly the same as in the gas phase [10]. In this contribution we will not consider further details like effects in the partial photoionisation cross section or like coverage dependent changes on the electronic structure, but concentrate on the spectra of the herringbone structure. As shown in Fig. 2 the most significant observation is the splitting of the 5 $\sigma$ , 3 $\sigma_g$  molecular ion states respectively. For N<sub>2</sub>/C the splitting is 0.45 eV, for N<sub>2</sub>/Ag(111) it is 0.55 and for CO/Ag(111) it is 0.7 eV. A shoulder in the 4 $\sigma$  level of CO/Ag(111) indicates a split in that level, too. For N<sub>2</sub>/C, Ag the corresponding 2 $\sigma_u$  split is not observed, but may be a consequence of its low cross-section of the 2 $\sigma_u$  level. In the emission of the 1 $\pi$  ion state there is no indication for a splitting or shoulder at all.

### Theorie and Discussion

In order to understand the splittings in the 4 $\sigma$  (3 $\sigma_g$ ), 5 $\sigma$  (2 $\sigma_u$ ) levels at normal emission, we have used semiempirical tightbinding cluster calculations for various cluster models. For parallel aligned molecules the  $\pi$ - $\pi$  interaction (overlap) dominates and a split in the 1 $\pi$  level of about 1.8 eV is found. On the other hand when a T-shape alignment of the molecules within the cluster is considered, the  $\pi$ -overlap is minimized. However, the larger overlap of the  $\sigma$ -orbital in the T-shaped geometry causes a split in the 4 $\sigma$ , (3 $\sigma_g$ ), 5 $\sigma$  (2 $\sigma_u$ ) levels. For example, our calculations for a (CO)<sub>n</sub> cluster reveal a splitting in the neutral ground state of 0.39 eV (5 $\sigma$ ),

0.25 eV (4 $\sigma$ ) and is 0.53 eV (5 $\sigma$ ), 0.38 eV (4 $\sigma$ ) if final state screening is included.

Besides, the similar splittings for the 5 $\sigma$  (3 $\sigma_g$ ) ion states the systems in discussion here [N<sub>2</sub>, CO/C, Ag(111)] show even more similarities, when the dispersion of the 5 $\sigma$  (3 $\sigma_g$ ) level is considered. In Fig. 3 the binding energies of the observed peak maxima (or shoulders) are plotted as a function of the wave vector component parallel to the surface, i.e.  $k_{||} \sim \sqrt{E_{kin}} \sin \delta$  ( $E_{kin}$  is the kinetic energy of the emitted electrons,  $\delta$  is the angle of detection with respect to surface normal). For all surfaces, the azimuth of the substrate was along the  $\overline{\Gamma K}$  substrate direction. The dispersion is almost symmetric around  $\overline{\Gamma}$  for all systems investigated. The differences may be caused as the polarization vector of the incoming light is only in the quadrant determined by the positive  $\overline{\Gamma K}$  direction of the substrate. For N<sub>2</sub>/Ag(111) the 3 $\sigma_g$  level beyond that symmetry point again shows a splitting.

The similarities in the dispersion curves are documented not only in the common splitting at  $\overline{\Gamma}$  as forementioned, they also show another symmetry point (1/3  $\overline{\Gamma K}$ ) of the substrate SBZ. This symmetry point is in accordance with the substrate distances  $a$  at 1/3  $a$  (graphite:  $a = 4.29$  Å; Ag(111):  $a = 4.99$  Å) for all three systems.

As the N<sub>2</sub>/C system has been studied by LEED [4, 5] and NSS [3], the evidence for a herringbone structure as determined by these techniques may be used as the basis to explain the results of ARUPS as reported here. Starting with the cluster models mentioned earlier, an ab initio calculation of the 2D bandstructure of an isolated N<sub>2</sub> layer forming a herringbone structure has been performed. The geometric arrangement is such that 2 molecules normal to each other form the unit cell. The next neighbor distance (center of mass) of 4.29 Å is one basis vector and is determined from the LEED data. Further details of that calculation are published elsewhere [11]. The calculated splitting at  $\overline{\Gamma}$  amounts to 0.30 and 0.23 eV for 3 $\sigma_g$  and 2 $\sigma_u$ , respectively. The 25 percent smaller splitting for 2 $\sigma_u$  is due to larger 2s components in the wavefunction. This probably can also explain

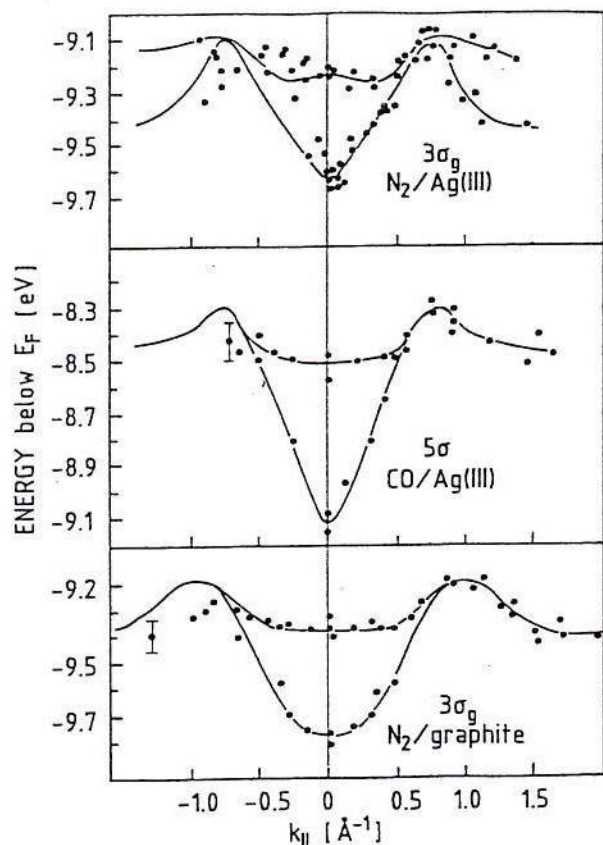


Fig. 3

Experimentally determined dispersion of the molecular level at lowest binding energy for N<sub>2</sub>/Ag(111) (3 $\sigma_g$ ), CO/Ag(111) (5 $\sigma$ ) and N<sub>2</sub>/graphite (3 $\sigma_g$ ) along the  $\overline{\Gamma K}$  direction of the substrate

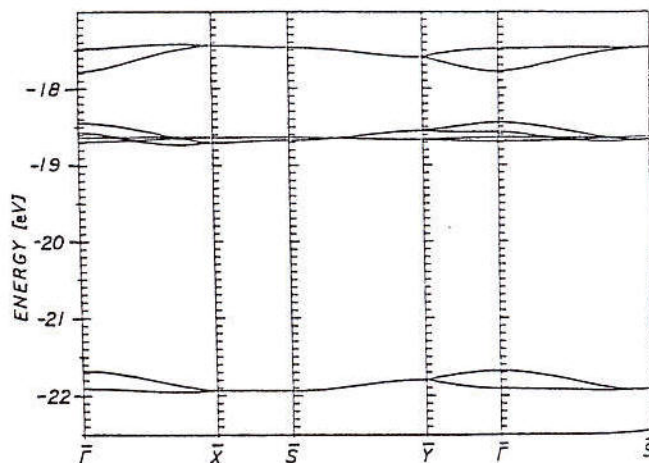


Fig. 4

Calculated band structure of an isolated N<sub>2</sub> layer ordered in the herringbone structure with the distances as observed for N<sub>2</sub>/graphite. The dispersion is shown along various symmetry lines within the rectangular surface Brillouin zone



why it is not resolved in the experimental spectrum. The resulting bandstructure along the main symmetry lines is shown in Fig. 4. Compared to our experimental data, the overall agreement is excellent, despite the coexistence of three possible domains. The calculation shows the splitting in the two  $\sigma$  levels at  $\bar{\Gamma}$ . For the  $2\sigma_u$  level the splitting is too small to be resolved experimentally.

Agreement is achieved also at the symmetry points S and H, where theory predicts that the levels are degenerated. The size of the splitting at  $\bar{\Gamma}$  is somewhat larger in experiment than expected from the calculation. Further computational improvement like variation of the angle between the molecules as well as variation of the next neighbor distance will give further insight in the details of this ordered phase.

### Summary

In summary, experimental and theoretical work established that an ordered herringbone structure exists for N<sub>2</sub> when adsorbed on graphite in accordance to LEED [4, 5] and NNS [3] work. Furthermore, the similarities observed for the spectra and dispersion of the  $5\sigma$  ( $3\sigma_g$ ) ion states of CO and N<sub>2</sub> adsorbed on Ag(111) are consistent with the existence of a similar ordered phase on this metal single crystal surface.

In the following we will discuss some of the consequences of the present work. From the viewpoint of ARUPS it is interesting to note that the size of the observed dispersion for a given level does *not* depend on the adsorbate substrate interaction. Dispersions around 0.7 eV have been observed for CO chemisorbed on transition metals [6, 12] as well as for noble gas atoms physisorbed on a variety of metals [7].

Another significant meaning of the work presented here is the fact that techniques forced to use high surface area polycrystalline materials as substrates (NNS, LEED, specific heat — isothermes, isobares) rank up to all established surface science techniques by the use of well defined single crystal surfaces. Combining the experimental data with the symmetry properties of the herringbone structure as obtained in Fig. 3, we find that for N<sub>2</sub>, CO adsorbed on Ag(111) the next neighbor distance is 4.99 Å and is commensurable with the lattice constant as it is for N<sub>2</sub>/C. This value is quite different from that determined for N<sub>2</sub>/C (4.26 Å) and may be stabilized by that surface interaction, as discussed above.

From the numerous structures identified in LEED experiments, for N<sub>2</sub>/C beside the in plane herringbone structure already mentioned, an incommensurate out of plane herringbone structure, with two molecules tilted away from the surface, is identified [14]. Since CO is a heteroatomic mol-

ecule the symmetry is lower and there exist several possible relative orientations thus causing the existence of only one glide plane. Understanding the absolute value of the splitting at  $\bar{M}$  may allow to identify the relative CO orientations. For CO/C beside the herringbone structure the so-called pin-wheel structure is established [12]. In this arrangement one upright standing molecule is surrounded by a ring (pin wheel) of five in plane oriented molecules. Within the SBZ there is one standing and three differently oriented in plane molecules. The LEED analysis also established that for all the observed structures the next neighbor distances do not change significantly. For N<sub>2</sub>, a tilting out of plane, and for CO, a standing up of one out of five molecules, are the driving forces for the phase transitions mentioned above.

Clearly, our ARUPS studies are not yet able to differentiate between those phase transitions where only subtle changes in intermolecular distance occur. However, the observed linewidths and dispersion curves may be blurred to a certain extent by the coexistence of both phases under our experimental conditions.

Nevertheless, we hope that the results presented here will influence the understanding of the fundamental properties of physisorption and stimulate further experimental and theoretical work of these very weakly bound systems.

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