

## Photoemission from Ordered Physisorbed Adsorbate Phases: N<sub>2</sub> on Graphite and CO on Ag(111)

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The measured two-dimensional band structure of physisorbed molecular monolayers has been used to determine the structure of the ordered phase. For the previously reported ordered herringbone structure of N<sub>2</sub> on graphite we observe a  $k$ -dependent splitting in the  $3\sigma_g$  level which is a consequence of the intermolecular interaction of the two molecules per unit cell. Our measured dispersion is consistent with the structure proposed by recent LEED calculations and with a semiempirical tight-binding calculation. For CO on Ag(111), which has not been studied by LEED, we find an orientationally ordered phase where there are two molecules per unit cell with the CO lying parallel to the surface.

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It is a common occurrence that chemisorbed molecules like CO or N<sub>2</sub> form ordered overlayers on transition-metal substrates. Angle-resolved photoemission has shown that the two-dimensional electronic bands formed by these molecular layers are consistent in periodicity with the real-space lattice,<sup>1-3</sup> and with the notable exception of weak chemisorption<sup>4</sup> the magnitude of the dispersion is given fairly accurately by an independent-particle calculation.<sup>2</sup> The normal bonding configuration for these chemisorbed molecules has the molecular axis perpendicular to the surface.<sup>3</sup> Only for the case of weakly interacting systems<sup>5,6</sup> (physisorption) has a bonding configuration with the molecular axis parallel to the surface been proposed. (We call this orientation "in-plane orientation.") At the present time there is no structural information for transition-metal-adsorbate systems with in-plane orientation. In contrast there are a tremendous amount of structural data available for physisorbed molecules with in-plane orientation (N<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and O<sub>2</sub>) on graphite.<sup>7-10</sup> Neutron diffraction,<sup>7</sup> LEED,<sup>8,9</sup> and x-ray diffraction<sup>10</sup> studies have provided clear evidence for a variety of different phases and orientational order-disorder transitions in these adsorbates dependent upon temperature and coverage. For N<sub>2</sub> on graphite at low temperature, an in-plane  $2(\sqrt{3} \times \sqrt{3})$  herringbone structure has been found. In this phase the centers of mass of the molecules occupy a  $(\sqrt{3} \times \sqrt{3})R 30^\circ$  structure. The orientational ordering is such that a  $(2 \times 1)$  superstructure is formed which has been theoretically predicted to be the most stable structure at this temperature.<sup>11</sup> Upon increase of the temperature the su-

perlattice disappears in an order-disorder transition.

In the present study we have used angle-resolved photoemission to study the electronic properties of in-plane-oriented N<sub>2</sub> and CO physisorbed on different substrates. We measured the dispersion,  $E(k)$ , curves, for N<sub>2</sub> on highly oriented pyrolytic graphite in the herringbone structure and correlated the measured "band structure" with the structural parameters known for this adsorbate. In comparison to the results of N<sub>2</sub>/graphite where the structure is known, we present data for CO/Ag(111) which show almost completely analogous behavior. Therefore we conclude that CO also forms an in-plane-oriented herringbone structure on Ag(111). Using semiempirical tight-binding wave functions, constructed from the constituent molecular wave functions, we calculate  $E(k)$  curves for the corresponding herringbone overlayer structures. These calculations allow us to interpret most of the experimental details on the basis of molecule-molecule interactions within the isolated layers.

Some typical photoemission spectra for the herringbone structure of N<sub>2</sub>/graphite are shown in Fig. 1(a). The  $3\sigma_g$ ,  $1\pi_u$ , and  $2\sigma_u$  molecular-orbital-derived ion states appear in the spectra at  $-9.5$ -,  $-10.7$ -, and  $-12.5$ -eV binding energies, respectively. For low adsorption temperatures and coverages in the monolayer range (bottom two curves) a characteristic splitting of  $\sim 0.4$  eV is observed in the  $3\sigma_g$ -derived ion state for all photon energies and collection angles near normal emission, i.e., near  $\bar{\Gamma}$  ( $k_{\parallel} = 0$ ). At large values of the parallel momentum  $k_{\parallel}$ , this splitting rapidly decreases

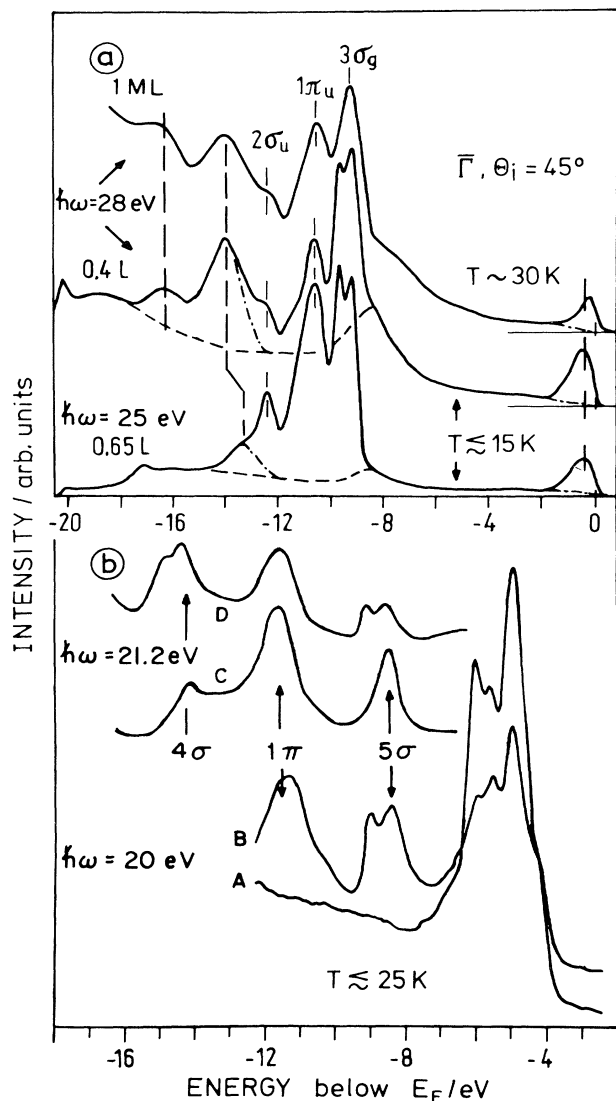


FIG. 1. Angle-resolved photoemission spectra of (a) physisorbed  $N_2$  on highly oriented pyrolytic graphite and (b) physisorbed CO on Ag(111). All of the curves except curve C of (b) were taken at normal emission ( $\bar{\Gamma}$ ). Curve C is close to the zone boundary of the CO/Ag(111) system ( $k_{\parallel} \sim 1 \text{ \AA}^{-1}$ ).

and vanishes near the boundary of the Brillouin zone.<sup>12</sup> The corresponding band dispersion for the  $3\sigma_g$  level is shown in Fig. 2 and is discussed below. Two additional points, however, are worth noticing in Fig. 1(a). Upon  $N_2$  adsorption not only do we observe extra emission from the molecular-ion states, but in addition find extra peaks right at the Fermi level as well as at the fixed kinetic energies of  $\sim 7$  and  $\sim 9.5$  eV above the vacuum level [dash-dotted curves, marked by dashed vertical lines, in Fig. 1(a)]. These structures are caused by umklapp scattering of graphite initial- and final-state emission features. In the com-

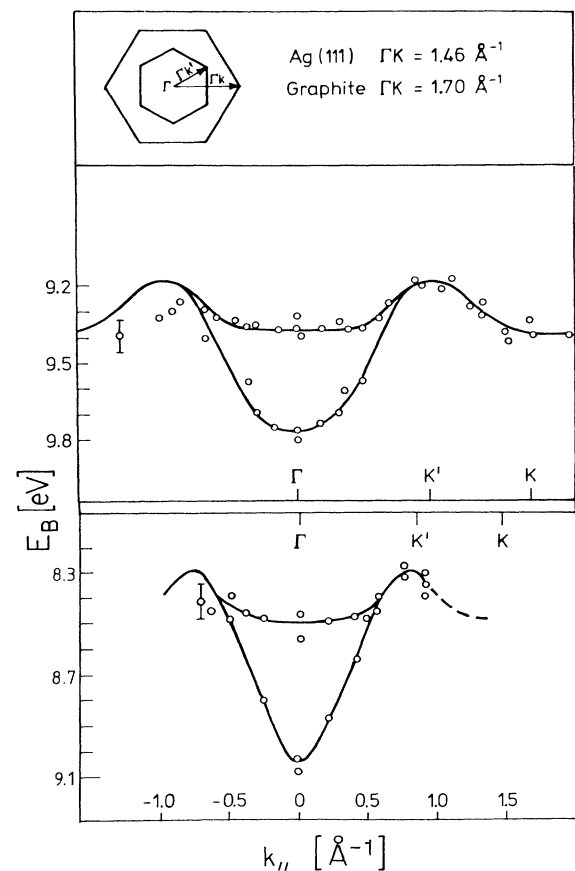


FIG. 2. Measured dispersion of the  $3\sigma_g$  level of  $N_2$ /graphite (top) and the  $5\sigma$  level of CO/Ag(111) (bottom). The measurements on Ag were made in the  $\bar{\Gamma}$ - $\bar{K}$  direction of the clean Ag. The inset at the top shows the Brillouin zone of the clean surface and the ordered physisorbed layer (Ref. 13). The  $3\sigma_g$  level of  $N_2$  is equivalent to the  $5\sigma$  level of CO.

mensurate  $(\sqrt{3} \times \sqrt{3})R 30^\circ$  structure, emission from the  $\bar{K}$  point in the uncovered graphite Brillouin zone can be diffracted by the center-of-mass scattering of the  $N_2$  molecules and hence will show up at  $\bar{\Gamma}$ , i.e., in normal emission. Using this observation we obtain an independent confirmation of the symmetry of the overlayer. The umklapp scattering persists when the temperature is raised above 27 K [curve C in Fig. 1(a)], where it is known that the orientational ordering disappears and the molecules become free rotators, centered at the same adsorption sites.<sup>8,9</sup> In this orientational order-disorder transition the splitting in the  $3\sigma_g$ -orbital-derived ionization disappears, as is expected for a transition from a nonprimitive (one molecule per unit cell) to a primitive unit cell based on the same  $(\sqrt{3} \times \sqrt{3})R 30^\circ$  (center of mass) overlayer. This observation is an additional confirmation of the interpretation given above for the origin of the splitting in the  $3\sigma_g$ -derived level.

Let us now turn to the results for the CO/Ag(111) system. In Fig. 1(b), spectra for this system are presented for two photon energies and two different measurement geometries. From a detailed study of the change in work function, the decrease in Ag  $d$ -band intensity, and the shifts of the binding energies of the CO peaks as a function of exposure, we know that after exposures of 4 L [1 langmuir (L) =  $10^{-6}$  Torr sec] the first monolayer is completed.<sup>14</sup> In Fig. 1(b) the spectra show the Ag  $d$  bands at  $-4$  to  $-8$  eV below the Fermi energy as well as the various ionic states of photoionized physisorbed CO ( $5\sigma$ ,  $1\pi$ , and  $4\sigma$ ). The spectra shown in Fig. 1(b) are taken at low photon energies where the splitting in the  $5\sigma$  is best observable since the  $5\sigma$  partial cross section increases towards lower photon energies.<sup>14</sup> Spectra taken after a 4-L exposure with 21.2-eV photons from a He resonance lamp are shown as curves *C* and *D*. Curve *D*, taken at  $\bar{\Gamma}$ , shows the 0.55-eV splitting in the  $5\sigma$  and also indicates a possible splitting in the  $4\sigma$ . Curve *C* is taken near the zone boundary where the splitting in both  $\sigma$  states has disappeared. The measured dispersion for CO/Ag(111) is shown in Fig. 2.<sup>15</sup> As in the case of the  $3\sigma_g$  level of N<sub>2</sub>/graphite, the splitting in the  $5\sigma$  level for CO/Ag(111) occurs symmetrically around  $\bar{\Gamma}$  and disappears rapidly towards the Brillouin-zone boundary. The antibonding component of the  $5\sigma$  level which appears at  $-8.5$  eV at  $\bar{\Gamma}$  shows little dispersion in the two-dimensional Brillouin zone. For both systems discussed here the relative energy positions of the center of the bands [ $\epsilon_0 = \int \epsilon(k) dk$ ] agree with the separations known from gas-phase CO and N<sub>2</sub>.

Let us summarize the dispersion features for both systems. The  $5\sigma$ - (CO) or  $3\sigma_g$ - (N<sub>2</sub>) derived bands show a splitting at  $\bar{\Gamma}$  which goes to zero at the zone boundary.<sup>13</sup> There is no measurable dispersion in the  $1\pi$  derived peak for either molecule. The  $4\sigma$  level of CO/Ag(111) shows an indication of a splitting at  $\bar{\Gamma}$  while there is no sign of an equivalent splitting for the  $2\sigma_u$  state (which corresponds to the  $4\sigma$  state of CO) of N<sub>2</sub>/graphite. Figure 2 displays the  $5\sigma$ -derived bands for both systems ( $3\sigma_g$  of N<sub>2</sub> corresponds to  $5\sigma$  of CO). The dispersion is symmetric about  $\bar{\Gamma}$  except for large negative  $k_{\parallel}$ . This discrepancy could result from misalignments of the experimental parameters. However, the deviations from the symmetrized solid lines are close to or even within the total experimental error. The dispersion curves show that the zone boundary for the ordered overlayer is at  $k_{\parallel} = 0.98 \text{ \AA}^{-1}$  for N<sub>2</sub>/graphite and  $k_{\parallel} = 0.84 \text{ \AA}^{-1}$  for CO/Ag(111).<sup>13</sup> When we take into account the  $k_{\parallel}$  values for the  $\bar{\Gamma}\bar{K}$  vectors of the clean substrates, we realize that these symmetry points occur right at  $\bar{\Gamma}\bar{K}/\sqrt{3}$ . This is clear evidence that the adsorbed layer has an orientation based on the  $(\sqrt{3} \times \sqrt{3})R 30^\circ$  structure. Our observa-

tions on CO/Ag(111) are consistent with the results for N<sub>2</sub>/graphite,<sup>8,9</sup> where for formation of the herringbone structure is established. The fact that both the overlayer structure as well as the structure of the substrate are reflected in the dispersion curves supports our proposal—that indeed the structure of the CO overlayer on Ag(111) is of the herringbone type. The angular and photon-energy dependence of the spectra can also be used to show that the CO/Ag(111) system is also an “in-plane orientation.”<sup>14</sup>

Even stronger support for this conclusion is obtained from a comparison of these data with a calculated band structure for CO and N<sub>2</sub>, that fully reflects the dispersion curves shown in Fig. 2. The two-dimensional band structure of an isolated molecular layer was calculated by use of a tight-binding scheme with nearest- and next-nearest-neighbor interactions. The molecular-orbital wave functions of the diatomic molecule under consideration were used as basis functions.<sup>2</sup> The procedure has been outlined before by Grueter *et al.*<sup>2</sup> and more details of this calculation will be published.<sup>14</sup> The intermolecular distances were taken from the LEED studies by Diehl and co-workers<sup>8,9</sup> for N<sub>2</sub>/graphite. The same spacing was used for the CO calculations displayed in Fig. 3 even though the CO overlayer on Ag(111) has a slightly smaller spacing. The structure for a CO herringbone pattern with two glide planes, restricting the relative orientation of the CO molecules in the overlayer to a head-tail arrangement, is shown at the top in Fig. 3.

There are several striking features of the calculated dispersion curves, especially when they are compared to the calculated dispersion for chemisorbed CO (see Fig. 10 of Ref. 2). First there is the splitting in the  $\sigma$  levels at  $\bar{\Gamma}$  for the herringbone structure which is missing in chemisorbed CO. This splitting is a result of having two molecules per unit cell for physisorbed CO compared to the one molecule per unit cell for chemisorbed CO.<sup>2,3</sup> The second difference is the absence of a shift of the  $5\sigma$  level towards the  $1\pi$  level in physisorbed CO. For end-on-bonded CO which is the only known form of chemisorbed CO the  $5\sigma$  level is stabilized by interaction with the substrate. The final and most difficult difference to explain is the small dispersion in the  $1\pi$  level in physisorbed in-plane-oriented CO. We will discuss the reasons for this behavior in detail elsewhere,<sup>14</sup> while a simple argument is presented here.

To illustrate the reason for the small  $1\pi$  dispersion in the herringbone structure, we have only to consider the symmetry of the tight-binding wave functions at the high-symmetry points of the surface Brillouin zone. Because of the presence of two molecules in the unit cell we have to form bonding and antibonding combinations of the wave functions of both molecules and then determine the dispersion.<sup>13</sup> For any pair of

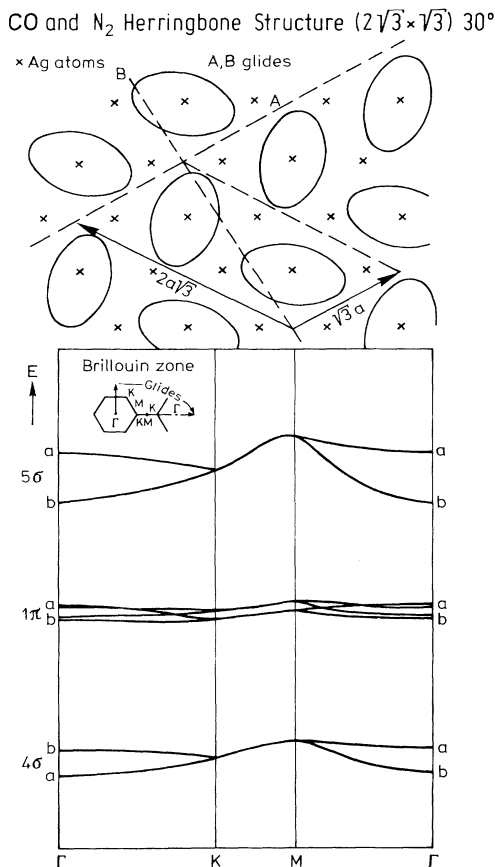


FIG. 3. Calculated two-dimensional dispersion of a layer of CO molecules in a herringbone structure. The structure is shown at the top (Ref. 13).

molecules with their axes perpendicular to each other, there is always the tendency for the overlap between the  $\pi$ -orbital wave functions to cancel out, whereas for molecules oriented parallel to each other they would add. This compensation therefore gives rise to the small dispersion observed in the  $\pi$  levels. For similar reasons, the coupling of the  $\sigma$ -derived wave functions leads to a splitting at  $\bar{\Gamma}$ , which is determined by the coupling of the two molecules in the unit cell. For the  $\sigma$  levels the interaction in the *neutral ground state* results in a splitting of 0.39 eV ( $5\sigma$ ) and 0.25 eV ( $4\sigma$ ) at  $\bar{\Gamma}$ .

In summary, we have illustrated that there is a well-defined two-dimensional band structure in physisorbed layers and that this band structure can be used in conjunction with simple tight-binding calculations to determine the structure of these weakly bound layers. For CO/Ag(111) an in-plane orientationally ordered herringbone structure is proposed in close analogy to  $N_2$ /graphite. The comparison of the data for these two systems gives clear evidence that two-dimensional phase transitions can be observed for heteroatomic

molecules as well as for molecules with axial symmetry, physisorbed on well-defined single-crystal metal surfaces. It is very interesting to note that the single-particle picture for dispersion works as well for ordered layers of physisorbed molecules as it does for strongly chemisorbed molecules. Yet the single-particle picture breaks down in the intermediate coupling regime of weak chemisorption.<sup>4</sup>

The CO/Ag(111) data have been taken while one of us (D.S) was at the Fritz-Haber Institut der Max-Planck Gesellschaft. The experimental assistance of A. Gutmann and the staff of the BESSY storage ring as well as the support of K. Jacobi through the Bundesministerium für Forschung und Technologie project No. 232 JA is acknowledged. For the  $N_2$ /graphite experiments the assistance of B. Tonner, the support of the staff of the Synchrotron Radiation Center (Stoughton, Wisconsin), as well as the financial support by the National Science Foundation through the Materials Research Laboratory program under Grant No. DMR-82-16718, and also by the Gas Research Institute are gratefully acknowledged. One of us (H.J.F.) acknowledges the support of the Deutsche Forschungsgemeinschaft.

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<sup>12</sup>Note that in the highly oriented pyrolytic graphite, which was kindly supplied by J. E. Fisher, these boundaries are somewhat smeared out by averaging over the in-plane polycrystallinity of the substrate.

<sup>13</sup>The hexagonal two-dimensional Brillouin zone of the physisorbed layer is a result of the superposition of the three domains of a rectangular Brillouin zone.

<sup>14</sup>D. Schmeisser, A. Gutmann, F. Greuter, E. W. Plummer, and H.-J. Freund, to be published.

<sup>15</sup>The splitting in the  $5\sigma$  level occurs only when the coverage is close to one full monolayer.