Orientational Ordering on a Corrugated Substrate: Novel Pinwheel Structure for N_2 Adsorbed on Cu(110)

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The structure and orientational ordering of N_2 molecules adsorbed on the Cu(110) surface is investigated in a combined experimental and theoretical study. Using He atom diffraction we find that monolayer N_2 forms a high-order commensurate phase with an oblique unit cell. Minimum energy calculations based on realistic potentials show that the unit cell contains seven N_2 molecules arranged in a novel type of pinwheel structure unexpected for linear molecules adsorbed on a smooth surface. Molecular dynamics simulations corroborate this structure and its remarkable thermal stability. [S0031-9007(97)02476-9]

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In contrast to adsorbed atoms, nonspherical molecules carry additional degrees of freedom related to their relative orientation on the surface. As a result, the corresponding phase diagram can be quite complex. Besides the positional ordering, various orientationally ordered superstructures may exist as well as new classes of order-order and order-disorder phase transitions. The simplest type of adsorbates to study orientational ordering are diatomic homonuclear molecules, such as H_2 or N_2. In fact, one of the best studied systems is molecular nitrogen adsorbed on the graphite (0001) basal plane [1].

Mean-field theory [2,3] has been used to study the ordering of point quadrupoles on a two-dimensional hexagonal lattice under the influence of a homogeneous crystal field (substrate holding potential V_c). A generic phase diagram is obtained in which four distinct orientationally ordered phases can occur depending on temperature and the relative strength of the holding potential and the quadrupole coupling constant Γ. (i) In the "two-in" herringbone phase, the molecules are lying flat with two possible in-plane orientations. (ii) In the "two-out" phase the molecules also form a two-sublattice herringbone structure, but the molecular axes are tilted by a finite angle with respect to the surface plane. (iii) At smaller $|V_c/\Gamma|$ a four-sublattice "pinwheel" structure is obtained, in which one pin molecule standing upright is surrounded by six molecules forming the wheel. However, each of the six wheel molecules belongs to two neighboring pinwheels such that the unit cell contains only four molecules. (iv) Finally, for large positive V_c (repulsive potential) a ferrorotational "ferro" phase with a single tilted molecule per unit cell is obtained.

The large number of experiments on N_2 and CO adsorbed on graphite has, indeed, revealed the occurrence of all three realistic structures (i)–(iii) [1]. Early LEED studies of N_2 on graphite [4,5] have provided the first clear evidence for a commensurate $(2\sqrt{3} \times \sqrt{3})R30°$ and a uniaxially compressed in-plane herringbone structure. At higher coverages an almost uniformly compressed triangular incommensurate phase was observed and the superstructure was assigned to a two-out herringbone lattice [6]. Subsequent neutron diffraction experiments corroborated these results [7]. However, a reinvestigation of the diffraction pattern at monolayer completion revealed that a four-sublattice pinwheel structure provided at least as good a fit to the diffraction intensities as the two-out herringbone structure [8]. Evidence for a four-sublattice pinwheel structure was also found for the compressed monolayer of CO adsorbed on graphite [9].

Besides the experimental investigations numerous theoretical studies have dealt with the structure and orientational ordering of N_2 on graphite [1]. Different approaches have been used such as energy minimization based on realistic potentials [10], Monte Carlo methods [11], and molecular dynamics simulations [12,13]. As a result, the commensurate and uniaxially compressed herringbone phases could be reproduced, and the existence of a pinwheel phase at monolayer completion was predicted [14]. Recently, the role of quantum effects on the herringbone order-disorder transition [15] and the structural disordering and melting [16] were also studied.

In this Letter we report on the structure of N_2 adsorbed on the highly corrugated, anisotropic Cu(110) surface. We find that the N_2 centers of mass are arranged along the substrate troughs in a hitherto unknown seven-sublattice pinwheel structure, demonstrating the strong influence of the substrate corrugation and anisotropy on the *orientational* ordering of linear molecules.

Our results are based on a helium diffraction study combined with energy calculations using realistic interaction potentials. The experimental setup is described in detail in Ref. [17]. A highly monochromatic He beam

($E_i = 18.3$ meV, $\Delta E = 0.2$ meV) is directed onto the sample and the scattered helium intensity is detected with a quadrupole mass spectrometer. Diffraction spectra were recorded by rotating the sample about an axis perpendicular to the scattering plane, changing simultaneously the angles of incidence and exit ϑ_i and ϑ_f of the He beam. Since the total scattering angle is fixed ($\vartheta_i + \vartheta_f = 90°$) the parallel wave-vector transfer for elastic scattering is given by $Q = \sqrt{2mE_i}\,(\sin\vartheta_i + \cos\vartheta_i)/\hbar$.

The sample is a high-quality single crystal Cu(110) surface with a miscut angle $<0.2°$. It was cleaned *in situ* by repeated cycles of sputtering with Ar^+ ions and heating to about 1000 K. The surface quality was routinely checked by He diffraction. The base pressure in the scattering chamber was in the low 10^{-11} mbar range.

Molecular nitrogen was adsorbed by exposing the cold Cu(110) surface ($T \sim 20$ K) to a nitrogen partial pressure. The N_2 coverage was controlled by monitoring the specularly reflected He intensity. Once the desired coverage was reached, the N_2 gas was pumped off. Then, the sample was annealed at around 28 K and, finally, cooled down to 20 K where most of the diffraction spectra were recorded.

In the entire coverage range up to monolayer completion and at temperatures below 32 K (where N_2 desorption sets in) the adlayer forms a stable high-order commensurate (HOC) structure [18]. Figure 1 shows a He diffraction profile recorded under an azimuthal angle rotated by 13.26° with respect to the $[1\bar{1}0]$ direction in real space. The complete diffraction pattern is shown as an inset in Fig. 1 together with the Cu(110) reciprocal unit cell. As indicated by the additional lines the unit cell in reciprocal space is derived from the substrate unit cell by a simple geometric construction. Therefore, the superstructure is commensurate. However, the N_2 unit cell is oblique and rotated with respect to the substrate high symmetry directions. Because of the C_2 symmetry of the Cu(110) substrate two equivalent domains can be formed on the surface. In fact, the measured diffraction spots result from the contribution of both domains.

The transformation from reciprocal space back into real space is straightforward and yields a $\left(\begin{smallmatrix}4 & 1\\ 1 & 3\end{smallmatrix}\right)$ unit cell for one of the two equivalent domains. This almost rhombic cell is indicated by solid lines in Fig. 2. The primitive vectors of the unit cell are rotated by $\tan^{-1}(\sqrt{2}/4) = 19.47°$ and $\tan^{-1}(3\sqrt{2}) = 76.74°$, respectively. Their lengths are almost equal ($\sqrt{18}\,a_{\mathrm{Cu}} = 10.82$ Å vs $\sqrt{19}\,a_{\mathrm{Cu}} = 11.12$ Å). Consequently, the superstructure has a quasihexagonal shape which, however, is in perfect registry with the substrate lattice. In this way, a compromise between the preferred two-dimensional net of the adlayer and the rectangular substrate lattice is reached, and the *symmetry frustration* is minimized.

The size of the superstructure unit cell is exactly 11 times that of the Cu(110) unit cell and, hence, much too large for being a *primitive* cell containing a single N_2 molecule. Consequently, the structure is *high-order* commensurate with several nonequivalent molecules per unit cell. From the van der Waals radii and the density of the N_2 monolayer structures on graphite (ranging between

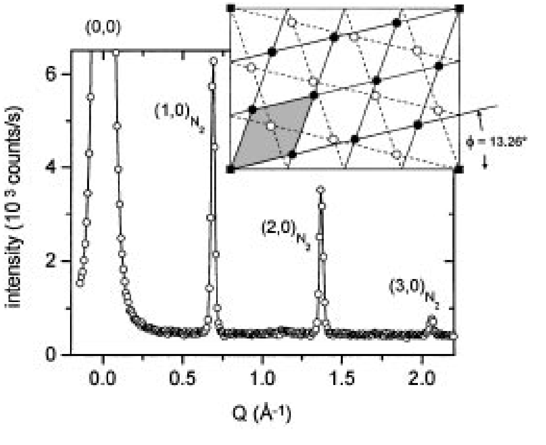

FIG. 1. He diffraction spectrum recorded from an N_2 monolayer adsorbed on Cu(110) along an azimuth $\phi = 13.26$ (measured against the $[1\bar{1}0]$ direction in real space). Incident He beam energy: $E_i = 18.3$, surface temperature $T = 20$ K. The inset shows the reciprocal unit cell of the Cu(110) substrate (outer rectangle) and of the HOC $\left(\begin{smallmatrix}4 & 1\\ 1 & 3\end{smallmatrix}\right)$ phase of monolayer N_2 on Cu(110) (hatched area). The circles indicate the positions of the observed diffraction peaks; filled and open circles (solid and dashed lines) are used to distinguish the contributions from the two equivalent domains.

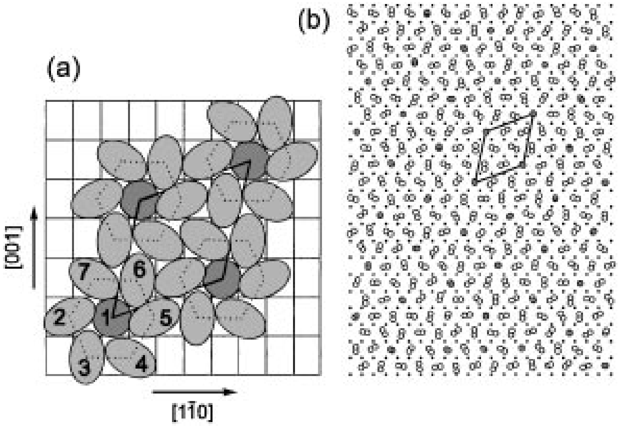

FIG. 2. (a) $\left(\begin{smallmatrix}4 & 1\\ 1 & 3\end{smallmatrix}\right)$ unit cell (oblique solid lines) with seven-sublattice pinwheel orientational order of the N_2 molecules adsorbed on Cu(110). A central upright molecule (1) is surrounded by six flat lying molecules (2–7). The molecules are arranged in a quasihexagonal lattice without leaving the potential troughs of the underlying rectangular Cu(110) substrate along the highly corrugated [001] direction. (b) Snapshot from the molecular dynamics simulation of the N_2/Cu(110) system at $T = 15$ K. Large circles indicate nitrogen atoms, protruding atoms are hatched for clarity. The rectangular Cu(110) lattice (small circles) and the $\left(\begin{smallmatrix}4 & 1\\ 1 & 3\end{smallmatrix}\right)$ unit cell (solid lines) are also indicated. A few defects in the orientational ordering are visible at the top and bottom of the simulation box.

0.064 and 0.071 molecules/Å^2) one can estimate that the unit cell should contain as many as 7 ± 1 N_2 molecules (corresponding to a density of 0.069 ± 0.009 Å^{-2}).

The questions that arise at this point are (i) how many molecules actually reside in the unit cell, (ii) how are they distributed within the unit cell, and (iii) what are their orientations? Unfortunately, these questions cannot be easily answered based on the He diffraction data alone [18,19]. The only qualitative information which can be inferred from the diffraction pattern concerns the possible orientational ordering of the molecules. Since all the diffraction peaks expected for the $\binom{4\,1}{1\,3}$ phase are actually observed and no indication of a systematic extinction of some of the spots has been found, we can exclude a herringbone-type ordering which would imply one or even two glide planes [4–6]. To solve the questions on the structural and positional ordering we have performed energy calculations based on realistic interaction potentials which were obtained from literature and checked against measured thermodynamic data for the N_2/Cu(110) system [20].

The total interaction potential $V(\mathbf{R}, \mathbf{\Omega})$ for the N_2/Cu(110) system is separated into two contributions, $V(\mathbf{R}, \mathbf{\Omega}) = V_{AA} + V_{AS}$, where V_{AA} and V_{AS} characterize the potential energies between N_2 molecules and between the adsorbate and the substrate, respectively. $\mathbf{R}$ locates the center of mass and $\mathbf{\Omega} = (\theta, \phi)$ the orientation of the N_2 admolecule assumed to be undeformable. We use a pairwise Lennard-Jones potential acting between the nitrogen atoms in different molecules. The set of parameters was taken in accordance to the $X1$ model of Murthy *et al.* ($\epsilon_{\mathrm{N-N}} = 3.14$ meV, $\sigma_{\mathrm{N-N}} = 3.318$ Å) [21]. Electrostatic contributions are included by an appropriate three point charge distribution model with two charges equal to -0.405 a.u. at the nitrogen sites and one charge equal to $+0.810$ at the center of the bond [21].

The adsorbate-substrate potential V_{AS} is mainly determined by dispersion-repulsion interactions [22] which were modeled by summing pairwise Lennard-Jones N-Cu potentials. The potential parameters were obtained from combination rules using $\epsilon_{\mathrm{Cu-Cu}} = 3.40$ meV and $\sigma_{\mathrm{Cu-Cu}} = 4.187$ Å which in turn are deduced from the known Xe-Xe and Xe-Cu potentials [22]. In this way we find $\epsilon_{\mathrm{N-Cu}} = 3.27$ meV and $\sigma_{\mathrm{N-Cu}} = 3.753$ Å.

Using the above interactions the potential energy map of a single N_2 molecule on the Cu(110) surface was calculated by optimizing the binding distance and the molecular orientation at each position within the surface unit cell. As a result, a highly anisotropic corrugation of 13 meV along the [001] direction and only 1 meV along the close packed $[1\bar{1}0]$ direction is found. In a second step, various high-order commensurate structures with different packing density varying ranging between 0.054 and 0.082 Å^{-2} have been minimized with respect to the total binding energy by varying all positional and orientational coordinates of the molecules in the unit cell independently using first a gradient approach. The results were then checked using simulated annealing to ascertain that, indeed, the overall minimum energy configuration was reached.

The energetically most favorable structure (at 0 K) turns out to be the one in which 7 N_2 molecules are arranged in a $\binom{4\,1}{1\,3}$ HOC unit cell in agreement with the experimentally observed superstructure. The molecules are arranged in a seven-sublattice pinwheel structure as shown schematically in Fig. 2(a). One upright molecule (number 1; $\theta_1 = 0°$) is surrounded by six flat lying molecules ($\theta_i = 90° \pm 0.3°$, $i = 2, \ldots, 7$) forming a pinwheel structure. The flat molecules coil around the pin molecule at alternating azimuthal angles $\phi_2 = \phi_5 = 25°$, $\phi_3 = \phi_6 = 85°$, and $\phi_4 = \phi_7 = 150°$. The six flat molecules are at the same height (3.4 ± 0.1 Å) above the surface, whereas the pin molecule sticks out further by 0.3 Å. Note that in the present case every wheel molecule belongs to a single pin, whereas in the classic four-sublattice configuration each wheel molecule is connected to two pins. We find that the average binding energy of -113 meV per molecule makes this configuration by far the most stable one.

The stability of this structure results from the fact that it provides an excellent compromise between the competing intermolecular forces ($V_{AA} \simeq -32$ meV per molecule) and the corrugation potential: while the N_2 molecules are close packed in a quasihexagonal arrangement with interatomic distances $R = 4.0 \pm 0.1$ Å, i.e., close to the equilibrium distance of the free molecules, they all lie within the troughs of the substrate holding potential along the highly corrugated [001] direction. This demonstrates how the geometry of a corrugated substrate may effect the structure and orientational order of an adsorbed molecular film.

Finally molecular dynamics (MD) simulations were performed to investigate the thermal stability of the positional and orientational ordering of the N_2 monolayer. The rectangular simulation box (56.1 Å × 79.2 Å) was chosen to be commensurate with the $\binom{4\,1}{1\,3}$ lattice and contained 308 N_2 molecules adsorbed on the rigid Cu(110) substrate. For a surface temperature of 15 K Fig. 2(b) shows that the molecules are arranged in a quasihexagonal structure with almost perfect pinwheel orientional order, in excellent agreement with the calculations of the minimum energy configuration at 0 K. MD calculations were also performed at higher temperatures revealing the remarkable stability of the seven-sublattice pinwheel structure. More specifically, the angular distribution functions for the orientation of the molecular axis both with respect to the surface normal and within the surface plane show characteristic peaks at those angles expected from the structural model in Fig. 2(a) with the correct relative population. Increasing the surface temperature up to 30 K the distribution functions are not significantly altered except for a broadening of the peaks.

This remarkable stability of the N_2 structure is also in agreement with experiment: no characteristic extinction of any of the main diffraction spots associated with the N_2 superlattice was observed as a function of the surface temperature. In the accessible range between 20 and 32 K the diffraction intensities of the various spots exhibit a smooth Debye-Waller type decrease, although with different "effective" Debye temperatures. From this we conclude that there is no abrupt order-disorder transition as observed, for instance, for N_2 monolayers in the herringbone structure on graphite [4]. However, the different slopes (effective Debye temperatures) could originate from a continuous change of the structure factor, e.g., due to a broadening of the angular distribution functions with increasing surface temperature as observed in the MD simulation. A detailed discussion of the positional and orientational order parameters deduced from the MD simulations will be given in a forthcoming article [20].

In conclusion, we have shown that a monolayer of N_2 adsorbed on the highly corrugated, anisotropic Cu(110) surface forms a remarkably stable, high-order commensurate phase with an oblique $\left(\begin{smallmatrix}4 & 1\\ 1 & 3\end{smallmatrix}\right)$ unit cell. Total energy calculations and MD simulations based on realistic interaction potentials show that each cell contains seven N_2 molecules. The molecules are arranged in a novel seven-sublattice pinwheel structure in which one upright molecule is surrounded by six flat lying molecules. To the best of our knowledge, such a structure has not been observed previously. In fact, it is not expected for linear molecules adsorbed on an uncorrugated substrate or a hexagonal lattice and, hence, demonstrates the strong effect of the surface anisotropy on the orientational ordering of linear molecules.

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