Structure of Physisorbed Overlayers of Dipolar Molecules: A Combined Study by Atomic-Beam Scattering and Molecular Dynamics

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Atomic-beam diffraction and molecular-dynamics calculations have been combined to study the structures of overlayers of the dipolar molecules CH_3F and CH_3Cl physisorbed on bare and xenon-plated graphite crystals. On the former substrate, CH_3F adopts a commensurate triangular lattice with one molecule per unit cell, whereas on the latter the unit cell doubles. On both substrates CH_3Cl is incommensurate with antiferroelectrically ordered molecules arranged in a uniaxially distorted structure.

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The structures and phase transitions occurring in monolayers of adsorbed molecules have been investigated by a variety of techniques, including computer simulation.[1-5] To date, dipolar molecules have received little attention.[6] In this Letter we report the structures of methyl fluoride (CH_3F) and methyl chloride (CH_3Cl) physisorbed on two well-characterized single-crystal surfaces: The basal plane of graphite (GR) and a monolayer of xenon adsorbed on the same substrate (Xe/GR).[7,8] By using CH_3F and CH_3Cl, we have changed the molecular size and polarizability, but kept the dipole moment essentially constant. There are many reasons for our choice of substrates. At $T \simeq 35$ K, which is our concern here, Xe is commensurate [$(\sqrt{3} \times \sqrt{3}) \times R30°$] with GR[7] and hence comparison of GR with the Xe/GR surface enables us to study the effect of enhanced substrate corrugation on the structure of the molecular overlayer. To probe the surface and overlayer structures, we have used the technique of helium-beam elastic scattering. The question we address is: How do physisorbed *dipolar* molecules order? A number of possibilities come to mind. These include domains of ferroelectrically ordered molecules, zigzag chains of ferroelectrically or antiferroelectrically ordered molecules, etc.[6] Anticipating our results, we find that, on graphite, CH_3F adopts a commensurate structure with one molecule per unit cell, whereas on the Xe-plated substrate the unit cell doubles. On the other hand, CH_3Cl is incommensurate with at least two molecules per unit cell on both substrates.

On the basis of molecular-dynamics (MD) calculations and analysis of the diffraction experiments, we conclude that CH_3Cl adopts a uniaxially distorted structure composed of antiferroelectrically ordered (AFEO) molecules, whose molecular symmetry axes are slightly canted with respect to the surface normal. The structure of CH_3F is less evident; the MD calculations suggest a

commensurate structure with ferroelectrically ordered (FEO) zigzag chains.

The experimental apparatus is described elsewhere.[9] Prior to deposition of the CH_3F layer, the cleanliness of the bare graphite single-crystal surface was checked. The diffraction pattern shown in Fig. 1(a) was taken with incident polar and azimuthal angles, $\theta = 53.2°$ and $\Phi = 30°$, respectively, while the incident He beam had an energy of 8.88 meV and a velocity dispersion less than 2%. The only in-plane diffraction channel open under these conditions is $(-2, -1)$. The well-resolved $(0,0)$ and $(-2, -1)$ peaks are indicative of a clean graphite surface. Following this experiment, a CH_3F beam with a flux of 2×10^{11} atoms mm^{-2} s^{-1} was directed onto the graphite crystal, while simultaneously monitoring the intensity of the specular He beam as a function of decreasing temperature. Loss of specular intensity at 85 K indicated the onset of CH_3F adsorption. As the overlayer forms, the specular intensity recovers, due first to the completion of the monolayer and then to the further lowering of the temperature. Before the specular intensity reaches a relative maximum, due to the onset of second-layer formation, the gas dosing of the surface is stopped, and the temperature is lowered to 35 K. Figure 1(b) shows the He diffraction pattern taken under identical scattering conditions (energy and incident angles) to the diffraction scan from bare GR. The appearance of well-resolved peaks, labeled $(-1,0)$, $(-2,0)$, and $(-3,0)$ indicate a larger periodicity than that of GR. The coincidence of the $(-3,0)$ peak with $GR(-2, -1)$ indicates registry of CH_3F with the substrate and a [$(\sqrt{3} \times \sqrt{3})R30°$] commensurate structure. This identification is confirmed by examination of the diffraction pattern for a Xe monolayer taken under identical conditions [see Fig. 1(c)]. The latter is known to adopt the commensurate [$(\sqrt{3} \times \sqrt{3})R30°$] structure.[7]
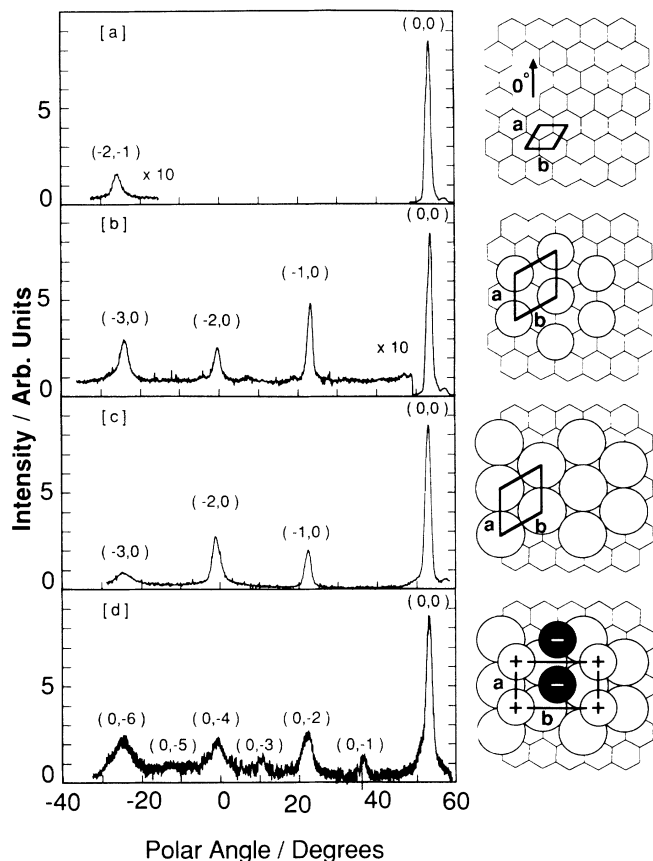
Since no satellite peaks are evident, we conclude that

FIG. 1. Helium diffraction from (a) bare graphite (GR), (b) CH$_3$F/GR, (c) Xe-coated GR, and (d) the bilayer system CH$_3$F/Xe/GR. The incident energy is 8.88 meV, $\theta = 53.2°$, and the surface temperature is 35 K. The diffraction peaks are labeled with reference to the primitive reciprocal lattice vectors of the topmost overlayer. Note that all overlayer lattices are rotated by 30° with respect to the GR substrate.

FIG. 2. Helium diffraction from (a) the monolayer system CH$_3$Cl/GR and (b) bilayer CH$_3$Cl/Xe/GR with the same experimental conditions as indicated in Fig. 1.

CH$_3$F/GR has a structure with only one molecule per unit cell. The two most likely structures involve either randomly oriented dipoles or uniformly ordered ones (i.e., all dipoles aligned at a fixed angle with the surface). It should be noted that although the diffraction-peak positions for Xe/GR and CH$_3$F/GR are coincident the relative intensities have changed. These changes in the scattered intensity are due to differences in the surface corrugation seen by the He beam.[10]

The last panel in Fig. 1 shows the diffraction pattern for a monolayer of CH$_3$F physisorbed on graphite precoated with a Xe monolayer. For this new situation, the relative strength of the admolecule-admolecule and admolecule-substrate interactions has changed drastically.[8] Indeed, the fact that the latter has weakened substantially, was confirmed by the observation that the adsorption of CH$_3$F on Xe/GR begins at $\simeq 65$ K instead of $\simeq 85$ K for CH$_3$F on bare GR ($\simeq 79$ K for Xe on GR). We see from Fig. 1(d) that this shift in the balance of

forces has produced a new structure. The three most intense peaks indicate a commensurate structure, while the three satellite peaks suggest a doubling of the unit cell. The interpretation of this diffraction pattern must allow for the fact that adsorption on graphite can occur on three distinct domains, rotated by 120° with respect to each other, and that the incident He beam is, likely, larger than a typical domain. The diffraction is, thus, a superposition of patterns from three such rotated domains. In the present context, it is difficult to distinguish between structures based on four molecules per unit cell (e.g., a pinwheel or AFEO zigzag chains) or uniaxial structures with two molecules per unit cell, such as FEO zigzag chains.[11]

We now turn to a discussion of the He diffraction results from the monolayer system CH$_3$Cl/GR shown in Fig. 2. The experimental conditions were identical to those used for the data shown in Fig. 1. All the peaks present in Fig. 2 are consistent with a uniaxial incommensurate structure, once due allowance has been made for each of the three possible rotated domains. We remark that the peaks $(-1, -1)$ and $(-2, -2)$ which appear in Fig. 2, are actually valleys between peaks that occur at $\Phi = 3.7°$ and are detected at $\Phi = 0$ only because of their finite width; a fact which was confirmed by examination of azimuthal scans (not shown). The lattice constants of the centered rectangular cell that generates this pattern are $a = 4.26$ Å, $b = 6.38$ Å, which compare

with the values $a = 4.26$ Å, $b = 7.38$ Å which would obtain for a commensurate structure $(CH_3F/Xe/GR)$. This reduction in the b lattice constant for CH_3Cl is consistent with an enhanced intermolecular attraction and a weakening of the role of the substrate. The diffraction pattern for $CH_3Cl/Xe/GR$ is also shown in Fig. 2. In marked contrast to the situation for CH_3F, there is no apparent change in periodicity.

So far we have not been able to arrive at any firm conclusion about the orientations of the CH_3F and CH_3Cl molecules in the overlayers. A natural way to proceed is to utilize MD calculations.[4,5] Two sets of potentials were used for each molecule. The first was constructed from the sum of Lennard-Jones potentials for CH_3-CH_3, F-F, and Cl-Cl taken from the literature.[12] The second set was derived from a combination of ab initio calculations and experimental viral-coefficient data.[13] To account for electrostatic interactions in both models charges were placed at the atomic sites of each molecule.[13] In view of our almost total ignorance of suitable molecule-surface potentials for the GR substrate, MD calculations are reported only for the case of Xe-plated GR. The Xe-GR and Xe-Xe Lennard-Jones potentials were taken from the literature.[14] The cross interactions were obtained via the combining rules for Lennard-Jones parameters, $\epsilon_{AB} = (\epsilon_{AA}\epsilon_{BB})^{1/2}$ and $\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2$.

The simulation system consisted of a patch of 168 dipolar molecules on top of 504 Xe atoms which, in turn, were in registry with 1512 graphite hexagons. Periodic boundary conditions were applied to the Xe/GR system in the (x,y) plane. A patch of dipolar molecules was used in order to circumvent the problem of long-range forces in this quasi-2D overlayer. The equations of motion were integrated in standard fashion with $T = 30$–50 K.

Before we studied the overlayers, the potentials were tested for bulk solid CH_3Cl. The calculated average potential energy for the first (second) potential was 23 (33) kJ/mol compared with an estimated experimental value of 27 kJ/mol.[13] Thus, the ab initio potential is too strongly bound by about 20%. In the case of physisorbed atomic overlayers, substrate-mediated (three body) interactions effectively reduce the adatom-adatom pair interactions by about 15%.[15] Since this effect has not been included in the present MD calculations, the first potential model is likely, fortuitously, a more realistic effective pair potential than the second. Accordingly, we only present results for the first model.

For the case of $CH_3F/Xe/GR$, calculations initiated with commensurate $[(\sqrt{3} \times \sqrt{3})R30°]$ molecules, either standing vertically or arranged in a herringbone, remained with centers of mass essentially commensurate and showed a clear preference for the FEO zigzag chains. Starting from similar initial conditions, the system $CH_3Cl/Xe/GR$ evolved to the incommensurate AFEO structure shown in Fig. 3, with $a = 4.25$ Å and $b = 6.75$ Å. In this structure, the molecules are canted
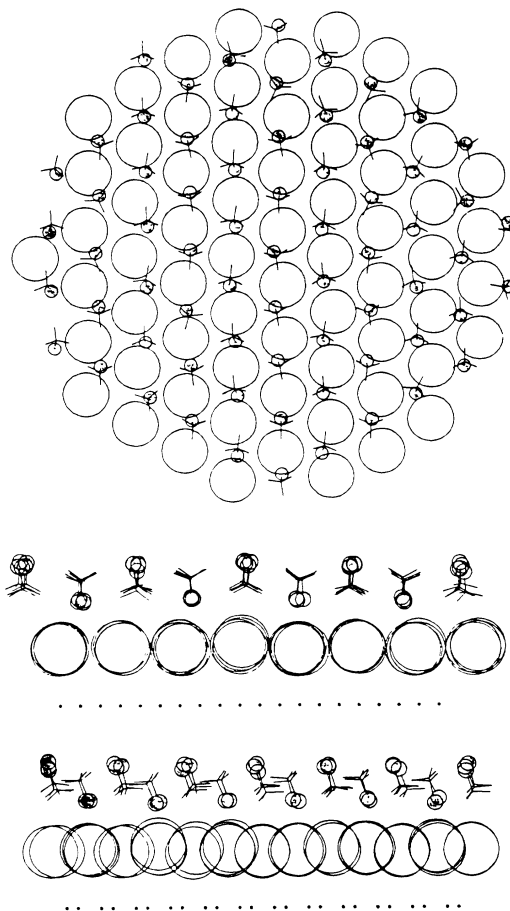

FIG. 3. Instantaneous configuration taken from the molecular dynamics calculations for the bilayer system $CH_3Cl/Xe/GR$ viewed from three mutually orthogonal directions (see text).

$\simeq 18°$, with respect to the surface normal along the a direction. Although the b parameter is 6% too large, the AFEO structure found in the MD calculations is, likely, closely related to the one responsible for the experimental diffraction pattern in the case of $CH_3Cl/Xe/GR$.

The difference in behavior between the chloride and fluoride molecules can be understood in terms of their intermolecular potentials. Since the polarizability of the chloride $(4.55$ Å$^3)$ is larger than that of the fluoride $(2.61$ Å$^3)$, the dispersion interaction is much stronger. Moreover, as regards to its polarizability and shape, the cloride behaves more like a diatomic, whereas the fluoride is almost spherical. These facts are reflected in the choice of potential parameters. Thus, although the dipole moments of the molecules are identical, they pack differently on the surface. Most important is the experimental observation that the separation between fluoride molecules is 4.26 Å but that for the larger chloride molecule it is much less. This is explained by the MD calculations that find the fluoride to be commensurate but the

chloride incommensurate. The reason for this is identified as the stronger tendency for the chloride to dimerize in an antiferroelectric fashion.

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