Surface Structure of Alanine on Cu(110) Studied by Fast Atom Diffraction

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We demonstrate that quantum scattering of fast atoms and molecules under grazing angles of incidence can be exploited to study the structure of organic molecules on metal surfaces. Making use of keV H and He atoms as well as H_2 molecules, the surface structures of the chiral amino acid alanine adsorbed on a Cu(110) surface is studied. We present a detailed investigation on the (3×2) phase of a monolayer of enantiopure and racemic alanine on Cu(110), revealing the formation of an elongated surface unit cell of $c(n \times 2)$ symmetry with $n = 3.16 \pm 0.04$ for the sticking out methyl groups of the alanine molecules.

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A few years ago, diffraction patterns were observed in the angular distributions of fast light atoms and molecules with energies up to some keV after grazing scattering from well-ordered surfaces [1–3]. In this specific regime of atomic collisions with solids, electronic excitations of target surface and projectiles [4] as well as the momentum transfer to surface atoms are widely suppressed [5–7] so that quantum coherence is preserved.

Fast atom diffraction (FAD) has been successfully demonstrated in studies on the structure of insulator [1–3], semiconductor [8], and metal surfaces [9,10], as well as on ordered thin films [11] and adsorbed atoms deposited on clean metal substrates [12,13]. Powerful features of FAD are the extreme sensitivity to the topmost surface layer, negligible modification of the surface structure, and no charging effects at insulator surfaces [3]. For example, vertical displacements of atoms from unreconstructed positions ("rumpling") for LiF(001) or MgO(001) surfaces could be determined with unprecedented accuracy [14–17].

In this Letter we demonstrate that FAD can be employed to study surfaces of self-assembled organic molecules [18,19]. The attractive features mentioned above make FAD a promising new tool in this active field. Small amino acid molecules adsorbed on Cu surfaces can be considered as important model systems where chirality–the property that an object cannot be mapped onto its mirror image–is of particular interest [20–22]. We will discuss the adsorption of the amino acid alanine (CH_3–CH–NH_2–COOH) on a Cu(110) surface [23–31]. Alanine exists in the two enantiomers R alanine and S alanine, where we will focus here on results for the racemic (equal) mixture of both species. It was an open issue whether or not the long-range order of such complex systems is sufficient to provide defined conditions for quantum scattering of fast atoms along low index directions in the surface plane. Furthermore, it was not clear to what extent quantum coherence was preserved in view of the variety of possible electronic excitations and energy transfer in collisions of fast atoms with adsorbed organic molecules.

A sketch of the collision geometry for grazing scattering of fast atoms and the recording of the diffraction pattern is shown in Fig. 1. H and He atoms as well as H_2 molecules (only results for H_2 projectiles will be presented here) with kinetic energies from 0.2 up to 2 keV were scattered under a glancing angle of incidence Φ_{in} ranging from 0.2° to 1.8° from a well-prepared clean and alanine covered Cu(110) surface. H_2^+ ion beams were collimated after neutralization in a gas target by three sets of sub-mm slits to a divergence of about 0.01° and directed onto the target surface in an UHV chamber at a base pressure in the upper 10^{-11} mbar domain. The preparation of the Cu(110) substrate was performed by grazing sputtering with 25 keV Ar^+ ions and subsequent annealing to about 800 K. Studies with a spot profile analysis low energy electron diffraction (LEED) system [32] showed a well-defined

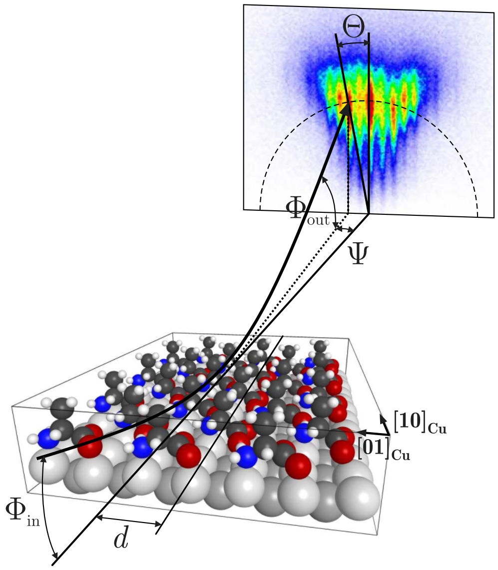

FIG. 1 (color online). Sketch of collision geometry for grazing scattering of fast atoms from crystal surface (surface plane). Angular distributions are recorded behind target normal to scattered beam (detection plane).

pattern of the unreconstructed phase of the Cu(110) substrate.

Two resistively heated quartz glass tubes filled with enantiopure S alanine (99.5%) and R alanine (99%) [33] were used to deposit alanine at a pressure of about 2×10^{-9} mbar. Angular distributions for scattered atoms were recorded by means of a position sensitive micro-channel plate (MCP) detector with delay line anode [34]. During deposition we could monitor with the MCP detector the intensity of specularly reflected projectiles which shows an oscillatory behavior for layer growth of ultrathin films [35,36] or dissociative adsorption of O_2 molecules on a Mo(112) surface [37]. For alanine adsorption we found a rapid decay of intensity with initial coverage followed by a maximum with about 50% of the initial intensity, which allowed us to control the formation of a complete alanine layer on the Cu(110) surface. Details on this topic will be outlined elsewhere [38].

The adsorption of alanine on Cu(110) has been studied in recent years using a number of standard surface analytical tools. For the coverage of the S- or R-enantiomers and the racemic (equal) mixture of both components, a phase diagram has been published [23,26] ranging from a disordered phase (phase I) at low coverages to an ordered monolayer film with (3×2) structure with respect to the Cu(110) substrate (phase IV) after annealing at about 480 K. In our experiments we could reproduce the different adsorbate phases and observe similar LEED patterns. The temperatures (measured via thermocouple attached to Cu crystal) for phase transitions and desorption agreed with those reported in [29,30], but were about 40 K lower compared to [23,26].

In Fig. 2 we show the structural model from [31] for the (3×2) phase for a monolayer alanine film where $[10]_{\mathrm{Cu}}$ and $[01]_{\mathrm{Cu}}$ denote directions of the basis vectors for the surface unit cell of Cu(110) and $[10]_{\mathrm{ala}}$ and $[01]_{\mathrm{ala}}$ of a $c(3 \times 2)$ unit cell with center symmetry. Along these basic directions, strings of atoms of substrate or molecular layer form low indexed channels which leads to steering of fast atomic projectiles during the collision with the surface, the so-called axial surface channeling [39,40].

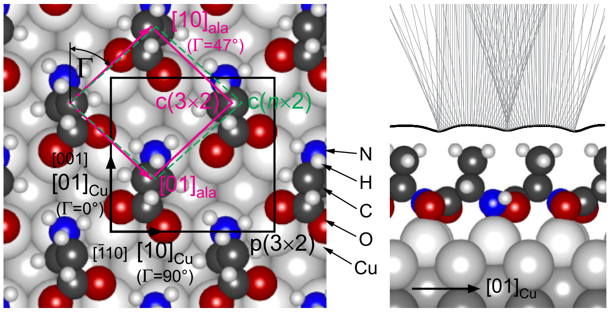

FIG. 2 (color online). Left: Structural model (top view) for $p(3 \times 2)$ phase of racemic alanine on Cu(110) from Ref. [33]; protruding methyl groups have $c(3 \times 2)$ or $c(n \times 2)$ symmetry. Right: Side view along $[10]_{\mathrm{Cu}}$ channel and sketch of resulting contour of interaction potential averaged along axial channel and projections of trajectories for scattering along $[10]_{\mathrm{Cu}}$.

In the regime of surface channeling, the motion of scattered atoms is characterized by a fast motion parallel to atomic strings with energies $E_{\parallel} = E\cos^2\Phi_{\mathrm{in}} \approx E$, with E being the total kinetic energy of the projectile atoms and Φ_{in} the grazing angle of incidence. The energy for the motion normal to the surface plane and atomic strings is $E_{\perp} = E\sin^2\Phi_{\mathrm{in}}$, which is for grazing scattering ($\Phi_{\mathrm{in}} \approx 1°$) of keV atoms in the sub-eV domain, i.e., from about 0.05 to 0.1 eV here. These energies are too low for penetration of the vacuum surface interface so that the fast projectiles are scattered in front of the topmost surface atoms. Because of the small angle with respect to the surface, the projectiles are steered by a large number of surface atoms and the effective interaction potentials result from an averaging over complete trajectories along the channels. The corrugation of this potential across the axial channels leads to an out-of-plane scattering as indicated in the right-hand panel of Fig. 2. This results in an azimuthal scattering by the angle Ψ or the angle of deflection in the detection plane Θ (cf. Fig. 1).

For quantum scattering, diffraction patterns are observed where the azimuthal angular positions Ψ_n for diffraction spots of order n follow from the simple Bragg relation

$$d_{[hk]} \sin\Psi_n = n\lambda_{\mathrm{dB}}, \tag{1}$$

where $d_{[hk]}$ is the lateral periodicity length transverse to the axial channel along $[hk]$, $\lambda_{\mathrm{dB}} = h/Mv$ the de Broglie wavelength associated with the center of gravity motion of a particle of mass M and velocity v, and h Planck's constant. Since for scattering of fast light atoms or molecules (H, H_2, He) λ_{dB} is more than 2 orders of magnitude smaller than typical periodicity lengths $d_{[hk]}$ at surfaces, Bragg peaks are separated by intervals of azimuthal angles of typically 0.1° only. However, in the regime of quantum scattering such small angular splittings can be resolved with well-collimated projectile beams.

In order to demonstrate the potential of FAD to study the structure of organic surfaces, we will concentrate on the (3×2) phase found for a monolayer coverage of alanine (phase IV) [23,26], where above temperatures of about 360 K (racemic alanine) up to 520 K (onset of desorption) an achiral organization is observed. As a representative example for our results, we present in Fig. 3 angular distributions for 0.4 keV H_2 molecules scattered from the surface of racemic alanine film annealed at a temperature of 410 K for 7 min (phase IVb). In the experiments the azimuth of the target surface was chosen such that the direction of the incident beam was parallel to $[10]_{\mathrm{Cu}}$ [3(a)], $[10]_{\mathrm{ala}}$ [3(b)], and $[01]_{\mathrm{Cu}}$ [3(c)]. For scattering along $[01]_{\mathrm{ala}}$, we found similar results as for $[10]_{\mathrm{ala}}$. Thus, three low indexed directions of the unit cell were probed. The data reveal defined diffraction patterns which shows that quantum scattering of fast atoms and molecules can also be applied to study the long-range order of organic films. Because for collisions under surface channeling

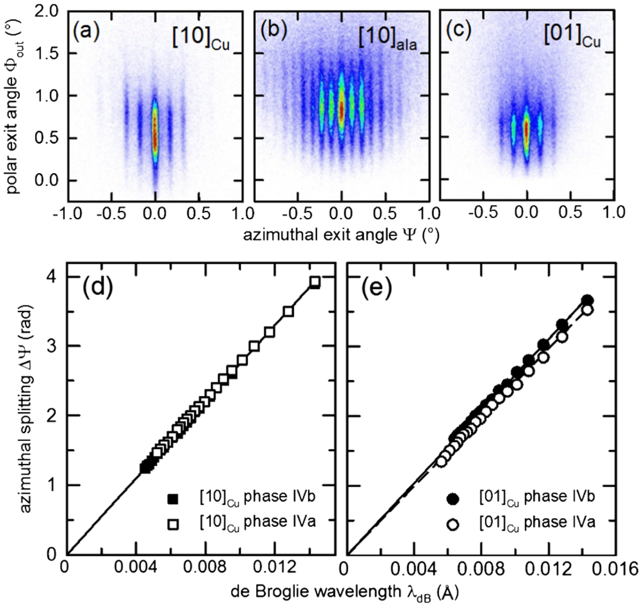

FIG. 3 (color online). Angular distributions as recorded with MCP detector for scattering of 0.4 keV H_2 molecules from surface of racemic alanine phase IVb along $[10]_{\mathrm{Cu}}$ (a), $[10]_{\mathrm{ala}}$ (b), $[01]_{\mathrm{Cu}}$ (c). (d),(e) Azimuthal splittings $\Delta\Psi$ between diffraction spots as function of λ_{dB} for scattering of H_2 molecules from surface of racemic alanine phase IVb (full symbols) and phase IVa (open symbols) along $[10]_{\mathrm{Cu}}$ (d) and $[01]_{\mathrm{Cu}}$ (e). Straight lines are best fit to data.

conditions projectiles are predominantly scattered from atoms of the topmost surface layer, positions of those atoms are probed by FAD. The patterns consist of elongated streaks which we ascribe to disorder of the film surface as also observed by STM [23]. This disorder affects the longitudinal shape of diffraction spots, and to a lesser extent the transverse coherence normal to the axial channels.

Using Eq. (1) the symmetry length $d_{[hk]}$ of the interaction potential across the axial channels can be derived from the azimuthal angles for positions Ψ_n of diffraction spots of order n. For a more accurate determination, $d_{[hk]}$ follows from a plot of the splittings between adjacent diffraction spots $\Delta\Psi = \Psi_{n+1} - \Psi_n \simeq \lambda_{\mathrm{dB}}/d_{[hk]}$ as a function of λ_{dB}. In Fig. 3(d) we have plotted the splittings of diffraction patterns $\Delta\Psi$ for scattering of H_2 molecules along the $[10]_{\mathrm{Cu}}$ azimuth as a function of λ_{dB}, which reveals the expected linear dependence with inverse slope $d_{[10]_{\mathrm{Cu}}}$. From a linear best fit to the data, we obtain $d_{[10]_{\mathrm{Cu}}} = (3.64 \pm 0.07)$ Å, which is in accord with the lattice constant for a copper crystal $a = 3.615$ Å. Since for a $p(3 \times 2)$ unit cell twice this value is expected, this result is in line with the also-discussed $pg(3 \times 2)$ [23,26–28], where the glide plane symmetry leads to $d_{[10]_{\mathrm{Cu}}} = a$. However, for the $[01]_{\mathrm{Cu}}$ direction [3(e)] with symmetry width $3a/\sqrt{2} = 7.67$ Å for a $p(3 \times 2)$ or $pg(3 \times 2)$ unit cell, we deduce from the data $d_{[01]_{\mathrm{Cu}}} = (3.86 \pm 0.07)$ Å $\approx 1.5a/\sqrt{2}$. This is consistent with a $c(3 \times 2)$ unit cell. Since for racemic alanine a $p(3 \times 2)$ unit cell contains two different enantiomers, whereas a $c(3 \times 2)$ unit cell contains only one molecule, a full center symmetry holds only for a part of the molecule.

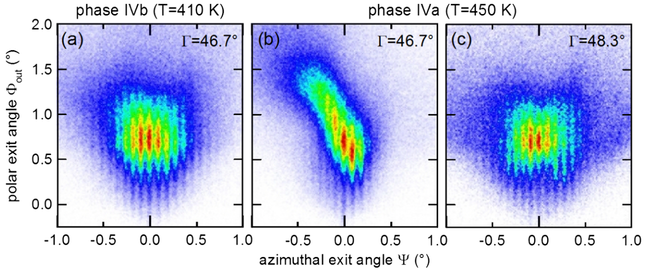

FIG. 4 (color online). Angular distributions for scattering of 0.7 keV H_2 molecules from surface of racemic alanine phase IVb (a) and phase IVa (b),(c) for azimuthal rotation from $[10]_{\mathrm{Cu}}$ by $\Gamma = 46.7°$ (a),(b) and $\Gamma = 48.3°$ (c).

The racemic film has the interesting feature that with annealing at temperatures above 420 K the structure of the film gradually converts from phase IVb with “true” (3×2) LEED patterns to the “distorted” phase IVa [23,29]. The LEED spots from the adsorbate are displaced in $[\bar{1}10]$ directions ($[10]_{\mathrm{Cu}}$ of surface unit cell) as always observed for phase IV of pure enantiomers.

Subsequent annealing cycles at temperatures around 420 K eventually reduced the splittings of the diffraction pattern for scattering along $[01]_{\mathrm{Cu}}$, as shown by the data represented by open circles in Fig. 3(e). From a linear fit to the data we derive $d_{[01]_{\mathrm{Cu}}} = (4.04 \pm 0.09)$ Å, while $d_{[10]_{\mathrm{Cu}}}$ remained unchanged [open squares in Fig. 3(d)]. For an enantiopure S alanine film we also find $d_{[01]_{\mathrm{Cu}}} = (4.00 \pm 0.08)$ Å. This finding can be explained by an expansion of the unit cell along $[10]_{\mathrm{Cu}}$ so that the topmost atoms of the alanine layer have a $c(n \times 2)$ unit cell referred to the substrate with $n = 3.16 \pm 0.04$.

In the regime of axial surface channeling, the intrinsic high resolution with respect to azimuthal angles can be used for detection of the expansion of the unit cell. This expansion in one dimension is accompanied by a slight azimuthal rotation of the diagonal direction of the unit cell. An azimuthal rotation of axial channels formed by topmost surface atoms or molecules by about 0.1° can be resolved in the experiment. The axial channel along the $[10]_{\mathrm{ala}}$ direction forms for a $c(n \times 2)$ phase an angle Γ with respect to $[01]_{\mathrm{Cu}}$ given by $\tan\Gamma = n/2\sqrt{2}$ (cf. Fig. 2). This amounts to $\Gamma = 46.7°$ for the undistorted phase and changes for $n = 3.16$ to $\Gamma = 48.2°$; i.e., the direction of the $[10]_{\mathrm{ala}}$ direction with respect to the substrate is changed for the transition from the undistorted to the distorted phase by an azimuthal angle of $\Delta\Gamma = 1.5°$.

In Fig. 4 we show angular distributions for scattering of 0.7 keV H_2 molecules scattered under $\Phi_{\mathrm{in}} = 0.7°$ from the surface of racemic alanine. The data displayed in Fig. 4(a) were recorded after annealing of the film at 410 K. In this

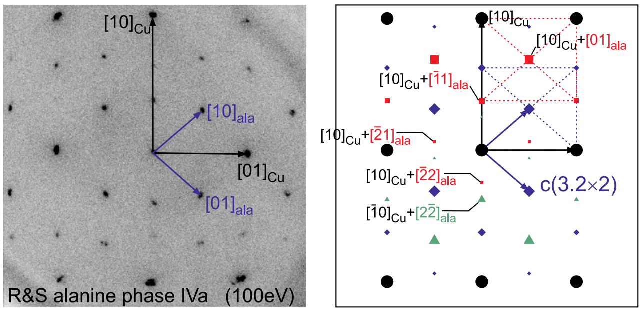

FIG. 5 (color online). LEED pattern (left) recorded for distorted phase IVa of racemic alanine compared with scheme for diffraction spots (right).

case a symmetric diffraction pattern is found for an azimuthal rotation of the target from $[01]_{\mathrm{Cu}}$ by $\Gamma = 46.7°$, which is in agreement with the direction of $[10]_{\mathrm{ala}}$ as calculated for the pure (3×2) phase (phase IVb). Further annealing of the film at 450 K leads to the diffraction pattern shown in Fig. 4(b), which shows the same signature of asymmetric shape as found for an azimuthal rotation of the target [41,42]. Thus, the shape of the angular distribution indicates that the direction of the probed axial channel was rotated during annealing. The effective angle of rotation of the axial channel can be simply obtained from an azimuthal rotation of the target, until the diffraction pattern is symmetric again [4(c)]. This is achieved for $\Gamma = 48.3°$. In view of the uncertainties inherent in this procedure, the results are in quantitative agreement with the expansion discussed above based on the symmetry lengths for the two other prominent axial channels of the unit cell.

With such a modified unit cell for the topmost atoms of the alanine film, it is straightforward to understand the "distortion" in the LEED pattern which was reported in the literature and attributed to a reconstruction of the substrate or to the presence of a large unit cell with local $p(3 \times 2)$ order [26,29,31].

The LEED pattern can be understood by multiple scattering of electrons from substrate and topmost atoms of the adsorbate layer. In Fig. 5 a LEED pattern recorded for the distorted phase IVa of racemic alanine is compared with a scheme for the diffraction spots. An elongated unit cell gives rise to a compressed reciprocal lattice in the $[10]_{\mathrm{Cu}}$ direction as sketched by (blue) diamonds. The (red) squares and (green) triangles are ascribed to multiple scattering from the substrate in the [10] and $[\bar{1}0]$ direction, respectively, and the adsorbate overlayer. This feature explains the "zigzag displacements" of the diffraction spots in the LEED images.

The surface structure observed by FAD is formed by the protruding methyl group of the alanine molecules, whereas the binding to the metal is achieved by the (deprotonated) carboxylic and amino group. In order to preserve the preferred near on-top adsorption sites of respective oxygen and nitrogen atoms as concluded from density functional theory calculations [27,29] and photoelectron diffraction studies [28], the positions of the methyl groups have to vary in the $[10]_{\mathrm{Cu}}$ direction compared to the rest of the molecule. This can be achieved by different adsorption footprints and modifications in molecular structure as discussed in the literature [29,31].

In conclusion, we observed diffraction patterns for grazing scattering of fast H_2 molecules from the surface of an ordered film of alanine molecules on a Cu(110) substrate. Our work demonstrates that the method of fast atom diffraction can be applied to studies on the structure of ordered films formed by organic molecules adsorbed on a metal substrate. From the analysis of data we found evidence for an expanded $c(3 \times 2)$ unit cell for the topmost atoms, i.e., of the methyl groups, which might explain the so-far insufficiently understood LEED patterns reported for this system in the literature.

The enhanced spacing of methyl groups indicates that their interaction is a key factor in the assembling of molecules [20]. This issue is also important for other organic molecules, and FAD with its extreme sensitivity to topmost atoms can provide complementary information on the surface structure compared to established methods. In general, low conductivity, charging effects, and radiation damage might affect the application of many standard surface analytical tools. In this respect, FAD has a great potential of being applied in studies on such systems without those constraints.

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