Unusual molecular orientation and frozen librational motion of C_{60} on Cu(110)

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Full-hemispherical angle-scanned x-ray photoelectron diffraction has been used to investigate the molecular orientation and librational motion of C_{60} molecules adsorbed on the Cu(110) surface. The molecules are found to face the substrate surface in an unusual bonding configuration, rotating their symmetry axes by a few degrees away from the high-symmetry directions of the Cu(110) substrate. Despite the asymmetric molecular orientation, the C_{60} molecules are immobile, i.e., they show no librational motion, up to temperatures well above the C_{60} sublimation temperature. [S0163-1829(99)01428-9]

In recent years, the adsorption of C_{60} on metal surfaces has been extensively studied, and important changes in the structural, vibrational, and electronic properties of the fullerene molecules due to the interaction with the surface have been determined.[1] By now, it is well established that C_{60} forms a chemical bond with metal surface atoms, which, depending on the electronic properties of the surface, can be more or less ionic or covalent in character.[2]

One valuable piece of information on the C_{60} metal interaction that became experimentally accessible only very recently is the molecular orientation of adsorbed fullerene molecules.[3] Since the charge distribution of an isolated C_{60} molecule is strongly modulated over the molecular cage,[4] it can be expected that its molecular orientation taken on a surface is intimately related to the details of the bonding interaction with the surface. Recently, the importance of the C_{60} molecular orientation has also been realized in the intriguing fullerene-based materials TDAE-C_{60} [TDAE =tetrakis(dimethylamino)ethylene] (Ref. 5) and A_3C_{60} (A = alkali metal).[6]

For monolayer C_{60} films adsorbed on single-crystal surfaces, we have previously shown[3] that a variety of molecular orientations is observed, ranging from the intuitively expected six-membered ring facing towards the surface on Cu(111) and Al(111) to the surprising double bond bridging between the close-packed rows of Cu(110) or a single edge atom facing towards the Al(001) substrate surface. This diversity of molecular orientations clearly highlights the subtle and yet still incompletely understood balance between molecule-molecule and molecule-surface interactions that governs the physics of fullerene adsorption on metal surfaces.

Motivated by the fact that C_{60} adsorption via a double bond bridging between the closed-packed rows of Cu(110) represents a rather asymmetric and unusual configuration, we have extended and refined our investigation of this system. The question whether the C_{60} molecules would undergo librational motion with increasing temperature or whether an orientational flip to a more favorable molecular orientation would occur—as recently observed for C_{60}/Ir(111) (Ref. 7)—has been addressed.

The experimental method of choice to determine the C_{60} molecular orientation is angle-scanned x-ray photoelectron diffraction (XPD).[8] It is based on the observation that, at electron energies above about 500 eV, the strongly anisotropic scattering of photoelectrons by the ion cores leads to a forward focusing of electron flux along the emitter-scatterer axis. Prominent intensity maxima in the angular distribution of photoelectrons can, therefore, often be identified with near-neighbor directions. At sufficiently high energies, XPD patterns therefore are, to a first approximation, a forward-projected image of the atomic structure around the photoemitter. For the case of Mg $K\alpha$-induced C 1s emission from C_{60} ($E_{kin}=970$ eV), a correlation of dominant intensity maxima in the diffraction pattern and C-C interatomic directions has clearly been demonstrated,[3] and the diffraction patterns thus represent a real-space "fingerprint" of the particular molecular orientation. Hence, XPD patterns from adsorbed monolayer C_{60} films allow a direct and unambiguous determination of molecular orientation.

The experiments were performed in a modified VG ESCALAB Mark II spectrometer[9] with a base pressure in the lower 10^{-11}-mbar region. Mg $K\alpha$-excited photoelectrons were analyzed with a 150-mm radius hemispherical analyzer. The Cu(110) crystal was prepared by cycles of Ar$^+$ sputtering and annealing to 840 K until the surface was judged clean and well ordered based on x-ray photoelectron spectroscopy and low-energy electron diffraction (LEED). High-purity C_{60} (Ref. 10) was deposited onto the Cu(110) surface by sublimation from a resistively-heated tantalum crucible. Highly-ordered C_{60} monolayers were obtained by depositing two or more monolayers onto the surface and subsequent annealing above the C_{60} sublimation temperature of 575 K for a few minutes. In agreement with previous
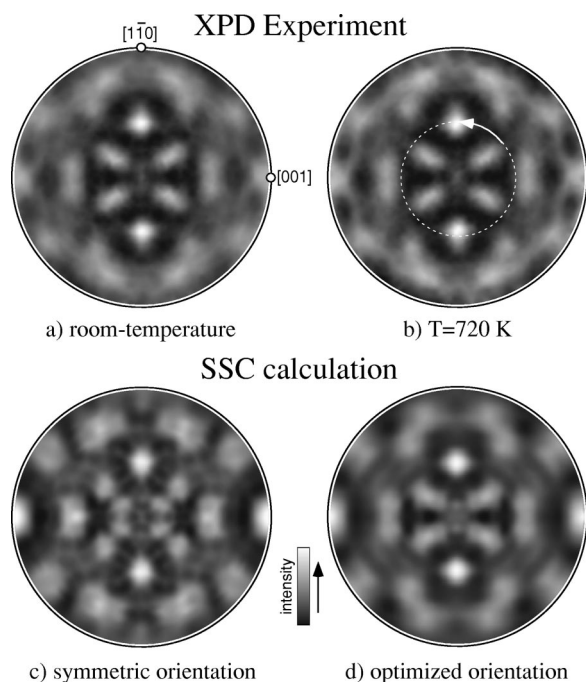
FIG. 1. C 1*s* XPD patterns ($E_{kin} = 970$ eV) from the C_{60} monolayer on Cu(110). (a), (b) Experimental patterns taken at RT and with the sample held at 720 K, respectively. (c) SSC calculation for a C_{60} molecule facing with a 5-6 bond towards the substrate, as schematically shown in Fig. 2. (d) SSC calculation for the optimized molecular orientation (see text).
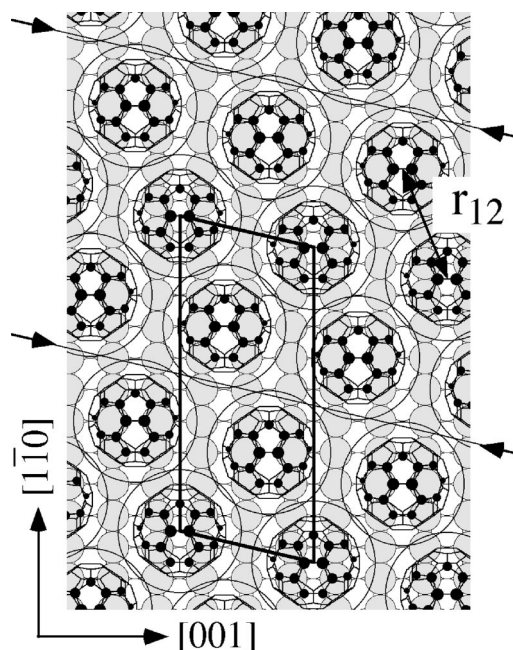

FIG. 2. Structural model for the C_{60} monolayer on Cu(110). For clarity, only the carbon atoms closest to the surface are shown as solid dots, with a size proportional to their proximity to the substrate surface. In order to indicate the distortion from a perfect hexagonal layer, circles whose radii corresponds to half the C_{60}-C_{60} NN spacing in bulk C_{60} (5.02 Å) are drawn around the molecules. Only one of the two possible domain orientations (unit cell indicated) and inequivalent azimuthal orientations of the molecules ($\pm 180°$) are shown. Arrows indicate the larger separation between adjacent rows occurring every three rows. The short $r_{12} = 9.6$ Å intermolecular distance is indicated.

observations,[11] we find that the C_{60}/Cu(110) monolayer system prepared in this way displays a sharp $\left(\begin{smallmatrix} 10 & 0 \\ \pm 1 & 3 \end{smallmatrix}\right)$ LEED pattern, where ± 1 corresponds to the two possible domain orientations (called $D1$ and $D2$ hereafter).

Experimental C 1*s* diffraction patterns from the monolayer C_{60} film on Cu(110) taken at room temperature (RT) and at 720 K are shown in Figs. 1(a) and 1(b), respectively.[12] The patterns have been azimuthally averaged exploiting the twofold rotational symmetry of the substrate and normalized to the smooth polar angle dependent background typical for adsorbate emission. The diffraction intensities are shown in stereographic projection and in a linear gray scale with maximum intensity corresponding to white. The orientation of the Cu(110) substrate surface as determined from Cu core-level XPD patterns (not shown) is indicated. Apart from minor differences in the background intensity due to thermal diffuse scattering, the two diffraction patterns taken at RT and at 720 K are identical, at least in what concerns the position of prominent features.

As these patterns are related in a straightforward way to the molecular orientation of the C_{60} molecules within the monolayer films,[3] it immediately follows that the molecules are identically oriented at either temperature. We have previously shown[3] that the RT diffraction pattern of Fig. 1(a) stems from C_{60} molecules facing with a 5-6 bond towards the Cu(110) surface (two inequivalent possibilities), and we therefore conclude that this unusual orientational configuration is stable up to at least 720 K. A single-scattering cluster (SSC) calculation[8] for this molecular orientation is shown in Fig. 1(c), and it can be seen that it reproduces the overall position and shape of the prominent forward-focusing maxima observed in the experimental patterns [Figs. 1(a) and 1(b)] fairly well.

Pedersen *et al.*[11] studied the adsorption of C_{60} on Cu(110) using scanning tunneling microscopy (STM) and found that a slightly distorted hexagonal overlayer was formed on the surface. From the STM pictures they concluded that the hexagonal structure consists of three equidistant parallel rows of C_{60} molecules running along the $[1\bar{1}3]$ direction, with a C_{60} periodicity of 11.2 Å along the rows. Every three rows, a slightly larger separation between the rows and a shift along the rows was observed. Furthermore, the center of the three parallel rows appeared about 0.1 Å lower than the neighboring rows, indicating that the molecules in the center row occupy another adsorption site than the ones in the two adjacent rows. Based on the assumption that the fullerenes will seek maximum coordination with the substrate, a structural model consisting of C_{60} molecules in twofold hollow positions as well as in (or close to) long-bridge positions was proposed. Complementing this model with our observation of the C_{60} molecules facing with a 5-6 bond towards the surface, we obtain a structural model as shown in Fig. 2. The unit cell as given by the LEED pattern contains three molecules, all of them facing with a 5-6 bond towards the surface. This molecular arrangement results in intermolecular distances that vary from as much as 9.6 Å (4% compression) to 11.1 Å (11% expansion) and in a density that is reduced by 6% with respect to that of a perfectly hexagonal close-
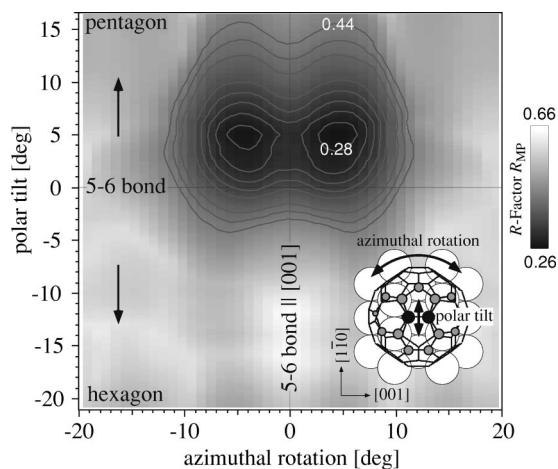
FIG. 3. R-factor plot obtained by azimuthal rotation and polar tilt of the C_{60} molecules away from the symmetric 5-6 orientation. Inset: Schematic drawing defining the angles used to describe the rotations. For clarity, only the carbon atoms closest to the surface are shown.

packed layer adopting C_{60} bulk nearest-neighbor (NN) distances.

The short intermolecular distance $r_{12} = 9.6$ Å (Fig. 2) led us to consider the possibility that the molecules might effectively increase their intermolecular C-C distances by slightly rotating away from the symmetric 5-6 orientation shown in Fig. 2. In order to examine this possibility, we have performed an extensive R-factor analysis comparing the experimental C $1s$ diffraction pattern [Fig. 1(a)] to SSC calculations, allowing the C_{60} molecules to rotate away from their genuine 5-6 orientation. The resulting R factors[13] are shown in Fig. 3, together with a schematic drawing defining the rotation and tilt angles used to quantify the molecular orientation. Indeed, tilting the C_{60} molecules by a few degrees around the [001] and subsequently around the [110] direction significantly lowers the R factor, and the best agreement with experiment ($R_{MP} = 0.26$) is obtained for a polar tilt angle of $4.5°$ and an azimuthal rotation of $\pm 4.5°$. The SSC calculation for these values [Fig. 1(d)] compares almost in every detail with the experimental diffraction pattern [Fig. 1(a)].

The optimum configuration of two NN molecules is schematically shown in Fig. 4. The two minima at $\pm 4.5°$ azimuthal rotation in the R-factor plot correspond to two different azimuthal orientations of the molecules [(+) and (−)] which in turn correspond one to each of the two different domain orientations ($D1$ and $D2$) of the $\left(\begin{smallmatrix} 10 & 0 \\ \pm 1 & 3 \end{smallmatrix}\right)$ structure. Only one domain orientation and its corresponding molecular orientation is shown in Fig. 4. The polar tilt of $-4.5°$ around the [001] direction inclines the molecule towards the bottommost five-membered ring, whereas the $4.5°$ azimuthal rotation around the [110] surface normal turns the bottommost 5-6 bond bridging between two close-packed Cu rows slightly away from the [001] direction. The former rotation might be rationalized by the resulting better-balanced C-Cu bond distance distribution, which might effectively increase the bond strength with the substrate. The effect of the azimuthal rotation, on the other hand, clearly is a maximization of the intermolecular C-C distances,[14] which might well be the driving force behind this peculiar arrangement.
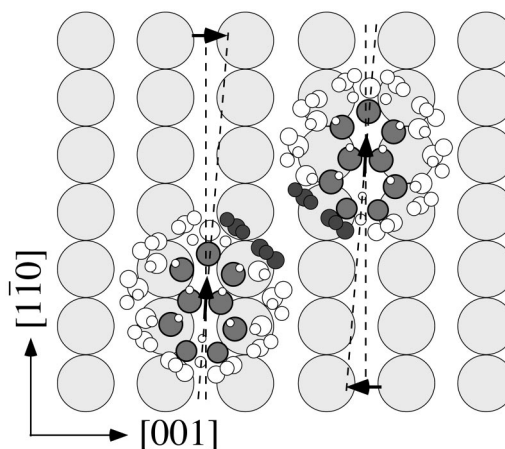

FIG. 4. Optimized molecular orientation of C_{60} adsorbed on Cu(110). Carbon atoms are shown as circles with a size proportional to their proximity to the substrate surface. The atoms belonging to the five-membered and six-membered rings closest to the surface are highlighted. Rotations away from the symmetric 5-6 orientation are indicated by arrows. NN molecules are facing each other with six-membered rings (solid dots), rotating the 5-6 bond closest to the surface by $4.5°$ away from the [001] direction and inclining their vertical axis by $4.5°$ towards the bottom five-membered ring.

In addition to its molecular vibrational modes, condensed C_{60} also exhibits external vibrations, including translational C_{60}-C_{60} vibrations and librational motions where the molecules rotationally rock in the potential of the surrounding crystal.[4] By means of inelastic neutron scattering, the latter
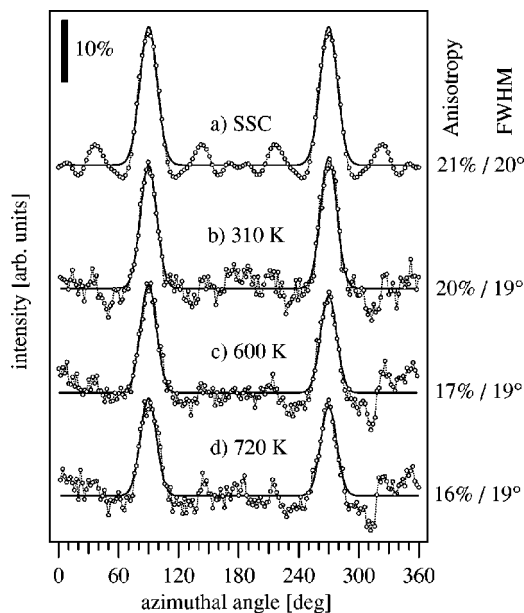

FIG. 5. Azimuthal photoelectron diffraction scans across the most prominent features of the C_{60}/Cu(110) diffraction pattern, as indicated by the dashed white line in Fig. 1(b). (a) SSC calculation, extracted from the pattern shown in Fig. 1(d); (b)–(d) experimental diffraction curves measured at different sample temperatures, as indicated. The black bar in the upper left corner gives a measure for the anisotropy of the data. For each curve, the width and anisotropy of the two main peaks have been determined by fitting two Gaussian peaks on top of a constant background (solid lines) to the data.

have been shown to occur around 2–3 meV.[15] Librational motions, i.e., hindered rotations, are also readily observed for molecules adsorbed on a surface, and its dynamics have been extensively studied using the electron stimulated desorption ion angular distribution method.[16] To our knowledge, the question whether adsorbed C_{60} molecules exhibit significant librational motions, however, has not yet been experimentally addressed. Using XPD, we have investigated the $C_{60}/Cu(110)$ system also with regard to this question. Azimuthal photoelectron diffraction scans across the most prominent diffraction features were measured with the monolayer $C_{60}/Cu(110)$ sample held at 310 K, 600 K, and 720 K and are shown in Figs. 5(b)–5(d), respectively. A calculation for the same polar emission angle performed for the optimized molecular orientation (Fig. 4) is shown in Fig. 5(a). It can be seen that the width of the two main peaks remains constant over the entire temperature range considered and is well reproduced by the calculation. The anisotropy slightly decreases from 20% at 310 K to 16% at 720 K. The anisotropy of the SSC calculation which considers a rigid molecule is 21%, only slightly larger than the experimental value for $T = 310$ K. This clearly rules out significant librational motion of the adsorbed molecules; rotational rocking of as little as two or three degrees would be detect-

ably reflected in the width as well as in the anisotropy of the diffraction features, as proven by the sensitivity of the R factors on molecular orientation shown in Fig. 3.

To summarize, using angle-scanned x-ray photoelectron diffraction, we have established a detailed picture of the subtle orientational arrangement of C_{60} molecules adsorbed on the Cu(110) surface. Most importantly, adsorption via the 5-6 bond is the preferred configuration for temperatures up to 720 K. However, the molecules are found to have their symmetry axes rotated away from the high-symmetry directions of the Cu(110) substrate by a few degrees. We have also observed similar asymmetries in other systems,[17] indicating that C_{60} adsorption in a highly symmetric orientational configuration is an exception rather than the rule. Despite the asymmetric orientation of the C_{60} molecules with respect to the underlying Cu(110) surface, no librational motion is observed up to temperatures close to the sublimation temperature of 730 K.

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[12] We have verified that the 4–6-h x-ray exposure necessary to collect these data does not induce any radiation damage to the adsorbed C_{60} molecules. LEED pattern and electronic structure as probed using ultraviolet photoelectron spectroscopy exhibit no changes even after prolonged measuring periods of up to 12 h.

[13] As in previous investigations, we have used the multipole R factor R_{MP}, which is based on the space of multipole coefficients rather than emission angles. For a definition of R_{MP}, see R. Fasel, P. Aebi, J. Osterwalder, L. Schlapbach, R.G. Agostino, and G. Chiarello, Phys. Rev. B **50**, 14 516 (1994).

[14] Assuming the twofold hollow position and the long-bridge position for the two NN C_{60} molecules (as shown in Fig. 2), the closest distance between carbon atoms belonging to two different molecules is 2.9 Å for the symmetric 5-6 bond orientation. This distance increases to 3.0 Å if the molecules rotate their axes by 4.5° ($+4.5°$ for domain $D1$ molecules, $-4.5°$ for domain $D2$ molecules) away from the high-symmetry directions as described in the text and schematically shown in Fig. 4. For azimuthal rotations of $-4.5°$ for domain $D1$ molecules and $+4.5°$ for domain $D2$ molecules, on the other hand, this distance decreases to 2.7 Å, confirming the attribution of the two azimuthal orientations $(+)$ and $(-)$ one to each of the two different domain orientations, $D1$ and $D2$.

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