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Orientation of Adsorbed C_{60} Molecules Determined via X-Ray Photoelectron Diffraction

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Although significant insight into fullerene-substrate interactions has come from recent surface science studies, to date there has been no unambiguous way to determine the molecular orientation of adsorbed C_{60} molecules. We show that photoelectron diffraction patterns from monolayer C_{60} films are directly related to the intramolecular structure of C_{60}. This allows for the first time a direct and unambiguous identification of the molecular orientation of the adsorbed fullerenes with respect to the substrate. A variety of molecular orientations is observed on different substrates.

Quantitative structural information is fundamental to the understanding of the physical properties of a solid, e.g., for the interpretation of spectroscopic results or as a starting point for theoretical calculations. The structure of solid C_{60} has been studied extensively using techniques like x-ray diffraction or neutron diffraction, and a quite detailed picture of its structural, electronic, and vibrational properties has been established by now [1]. Recently, much work has been carried out on fullerene-substrate systems, and important insight into electronic and vibrational energy levels has been gained [2–7]. However, the link between electronic and vibrational properties on one hand and structural properties on the other hand has still been missing. The question of molecular orientation in fullerene-substrate systems has resisted a solution by "conventional" techniques such as those mentioned above or low-energy electron diffraction. There have been a few reports of internal molecular contrast in scanning tunneling microscopy (STM) [8–10], but the inherent problem of tip-sample interaction renders the interpretation of these STM images far from obvious.

Because of the chemical sensitivity and the sensitivity to local order x-ray photoelectron diffraction (XPD) is a powerful technique for surface structural investigations [11]. It has been shown that full hemispherical XPD patterns provide very direct information about the near-surface structure [12,13]. 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 XPD pattern can therefore often be identified with near-neighbor directions. The scattering situation for a C_{60} molecule chemisorbed on a single-crystal surface is schematically shown in Fig. 1(a). All the 60 carbon atoms of the molecule act as photoemitters, and the photoelectrons are scattered from the surrounding ion cores. Because of the forward-focusing effect discussed above, intensity maxima are observed in directions corresponding to C-C interatomic directions [Fig. 1(b)]. The photoelectron angular distribution therefore is, to a first approximation, a forward-projected image of the atomic structure around the photoemitters. Analysis of the symmetry and positions of forward-focusing

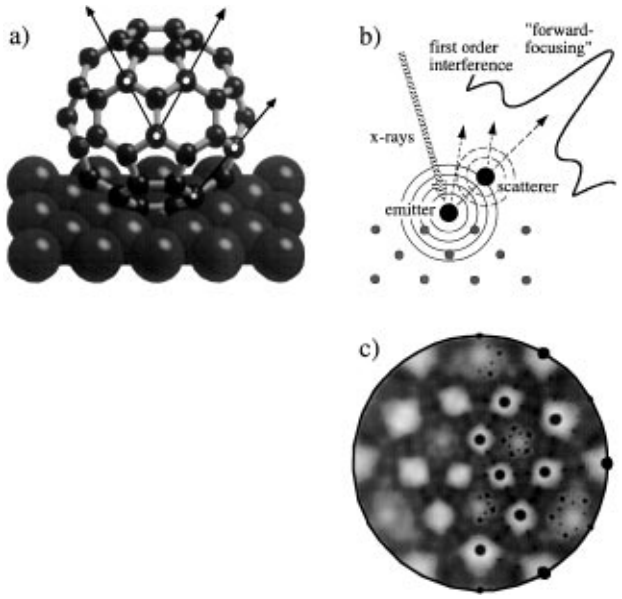

FIG. 1. X-ray photoelectron diffraction from chemisorbed C_{60} molecules. (a) When the surface is illuminated by x rays photoelectrons are emitted from each of the 60 carbon atoms within the molecule and scattered from the surrounding ion cores. (b) Because of the anisotropic scattering, the photoelectron intensity is forward focused along the emitter-scatterer directions. The photoelectron angular distribution therefore is, to a first approximation, a forward-projected image of the atomic structure around the photoemitter. (c) X-ray photoelectron diffraction pattern calculated for a C_{60} molecule facing with a 6-ring towards the surface, as sketched in (a). The photoelectron angular distribution is shown in stereographic projection and in a linear gray scale with maximum intensity corresponding to white. The center of the plot corresponds to the surface normal and the outer circle represents grazing emission along the surface. In the right half of this plot, the interatomic directions within the C_{60} molecule are indicated by black spots with sizes inversely proportional to the corresponding C-C distance. Correlation of dominant intensity maxima in the diffraction pattern and interatomic directions is observed, and the diffraction pattern thus represents a real-space "fingerprint" of the particular molecular orientation considered.

maxima thus permits a very straightforward structural interpretation of XPD data. Furthermore, detailed structural parameters can be determined by comparing the experimental XPD patterns to calculated ones, optimizing the structural parameters until best agreement is achieved. The relatively simple and efficient single-scattering cluster (SSC) formalism [11] has proven adequate in most cases [12,13], and specifically for other carbon allotropes [14]. Figure 1(c) shows an XPD pattern calculated for a C_{60} molecule facing with a six-membered ring (6-ring) towards the surface, as sketched in Fig. 1(a). In the right half of this plot, the interatomic directions within the molecule are indicated by black spots with sizes inversely proportional to the corresponding C-C distance. As expected, correlation of dominant intensity maxima in the diffraction pattern and interatomic directions is observed, and the diffraction pattern thus represents a real-space "fingerprint" of the particular molecular orientation considered. We show that full-hemispherical XPD patterns from adsorbed monolayer C_{60} films indeed allow a very direct and unambiguous determination of molecular orientation.

Experiments were performed in a VG ESCALAB Mark II spectrometer modified for motorized sequential angle-scanning data acquisition [13], and with a base pressure in the lower 10^{-11} mbar region. Photoelectron spectra and diffraction patterns were measured using Mg Kα ($h\nu = 1253.6$ eV) radiation with the samples kept at room temperature. Contamination free surfaces were prepared by standard Ar^+ sputtering and annealing cycles. C_{60} of 99.9% purity [15] was evaporated from a resistively heated Ta crucible while the crystal was maintained at room temperature. Monolayer C_{60} films were prepared by deposition of two or more layers of C_{60} and subsequent annealing of the sample to 320 °C. The purity of the C_{60} layers, as well as the coverage, was checked by core-level photoemission.

Experimental C 1*s* diffraction patterns from monolayer C_{60} films on Cu(111), Al(111), Cu(110), and Al(001) are shown in Fig. 2. Each adsorbate system gives rise to a unique and well-defined diffraction pattern. The patterns from C_{60} on Cu(111) and Al(111) [Figs. 2(a) and 2(b)] reveal sixfold symmetry with two sets of prominent maxima at ≈60° and ≈74° polar-emission angle, while the pattern from C_{60}/Cu(110) is clearly twofold symmetric, with two dominant maxima at ≈46° [Fig. 2(c)]. A fourfold symmetric pattern is obtained from C_{60}/Al(001), with four prominent maxima at a polar-emission angle of 47° [Fig. 2(d)]. As discussed above, the diffraction patterns of Fig. 2 are related in a straightforward way to the molecular orientation of the C_{60} molecules within the monolayer films. By symmetry arguments alone, restrictions to the possible molecular orientations can immediately be made. The fivefold rotational symmetry of the C_{60} molecule facing with a 5-ring towards the surface excludes this orientation for all the systems presented in Fig. 2. The twofold and fourfold symmetries of the patterns from C_{60} on Cu(110) and Al(001), respectively, also exclude adsorption on a 6-ring, which represents a configuration with threefold rotational symmetry, on these surfaces. Furthermore, it can be recognized that the patterns in Figs. 2(a) and 2(b) are very similar except for a 30° rotation, which indicates that on Cu(111) and Al(111) the molecules are facing with the same atom group towards the surface, but with azimuthal orientations differing by 30°.

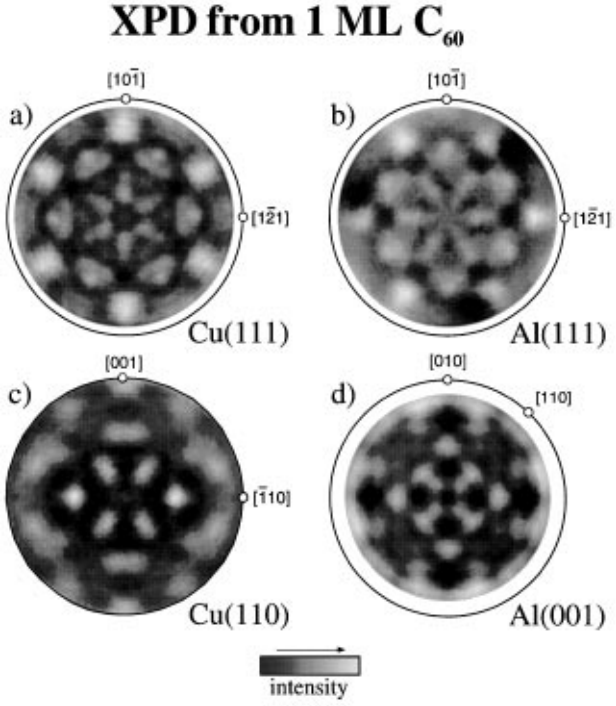

FIG. 2. Experimental C 1*s* x-ray photoelectron diffraction patterns (Mg Kα, $E_{\mathrm{kin}} = 970$ eV) from monolayer C_{60} films adsorbed on (a) Cu(111), (b) Al(111), (c) Cu(110), and (d) Al(001). The patterns have been azimuthally averaged exploiting the rotational symmetry of the respective substrate 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 substrate surface as determined from substrate core-level XPD patterns (not shown) is indicated.

In order to explain the diffraction patterns of Fig. 2, we have considered the five symmetric molecular orientations of a C_{60} molecule adsorbed on a surface, namely, a 5-ring or a 6-ring facing towards the surface, adsorption on two carbon atoms belonging to two 6-rings (6-6 bond) or to a 6-ring and a 5-ring (5-6 bond), and finally adsorption on a single carbon atom forming the edge between two 6-rings and a 5-ring. SSC calculations for these five molecular orientations have been performed using rigid C_{60} cage geometries. The SSC model used for photoelectron diffraction calculations is described in detail elsewhere [11], and we have used it in a form that contains spherical-wave scattering and the correct $s \rightarrow p$ angular

momentum final state in C 1*s* photoemission. The partial-wave scattering phase shifts δ_l for scattering at C atoms have been calculated by means of an algorithm which is based on the muffin-tin approximation [16]. Scattering phase shifts calculated for C muffin-tin potentials within the diamond or the graphite lattice have been verified to result in indistinguishable SSC calculations for C_{60}. A C 1*s* inelastic mean free path of 30 Å has been used for the calculations. The effective inner potential V_o responsible for the refraction of the photoelectron wave at the surface-potential step has been set to 5 eV. The possibility that a particular molecular orientation occurs in different azimuthal orientations depending on the symmetry of the substrate surface has been taken into account.

The whole set of calculations as well as the individual adsorption systems will be discussed in detail elsewhere [17,18]. In Fig. 3 we show a compilation of the SSC calculations corresponding to the experimental patterns of Fig. 2. We find that on Cu(111), the C_{60} molecules are adsorbed facing with a 6-ring towards the surface, in two azimuthal orientations differing by 60° [Fig. 4(a)]. The bonds within the 6-ring are found to be perpendicular to the close packed $\langle 10\bar{1}\rangle$ directions of the Cu(111) surface. This is consistent with the conclusions based on a STM study where threefold internal molecular contrast was observed [9]. On Al(111), where covalent bonding of the C_{60} molecules has recently been reported [5], the same molecular orientation as on Cu(111) is found, but with the difference that the bonds within the 6-ring are aligned along the close-packed $\langle 10\bar{1}\rangle$ directions of the Al(111) surface [Fig. 4(b)]. On Cu(110), adsorption takes place on a 5-6 bond aligned along the $\langle 001\rangle$ surface directions [Fig. 4(c)], whereas on Al(001) the C_{60} molecules are adsorbed facing with a single edge atom towards the substrate [Fig. 4(d)]. Four different azimuthal orientations corresponding to the 5-ring being oriented along the four $\langle 110\rangle$-like directions are observed. As can be seen by a comparison of Figs. 2 and 3, the calculations reproduce the experimental XPD patterns rather well, even though no structural refinement has been attempted up to this point. This is very promising in that also more complicated systems involving many inequivalent molecular orientations or some degree of orientational disorder might be successfully analyzed using XPD.

We have shown that full-hemispherical photoelectron diffraction allows an unambiguous determination of the molecular orientation of monolayer C_{60} films adsorbed on single-crystal surfaces. Adsorption on 6-rings, on 5-6 bonds, as well as on edge atoms has been found for C_{60} on Cu(111) and Al(111), Cu(110) and Al(001),

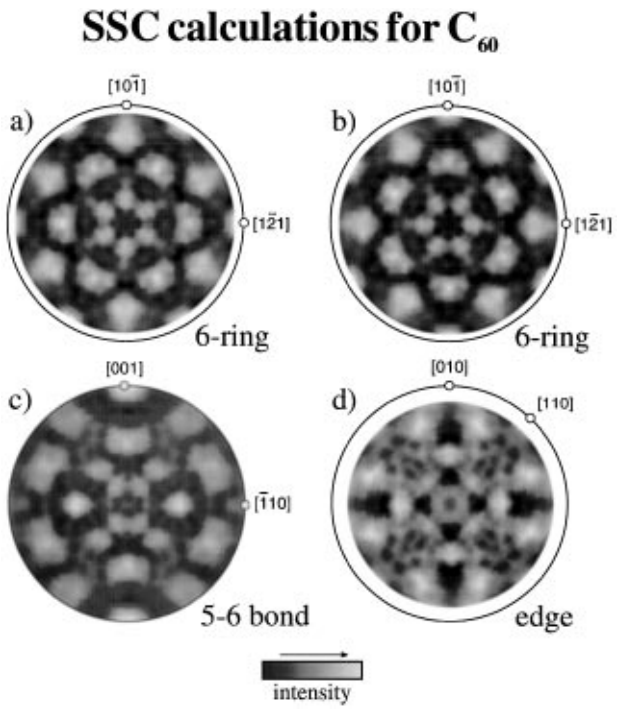

FIG. 3. Single-scattering cluster calculations reproducing the experimental XPD patterns shown in Fig. 2. The molecular orientations corresponding to these calculations are discussed in the text and schematically shown in Fig. 4. No attempt to optimize the structural and nonstructural input parameters in the calculations has been made.

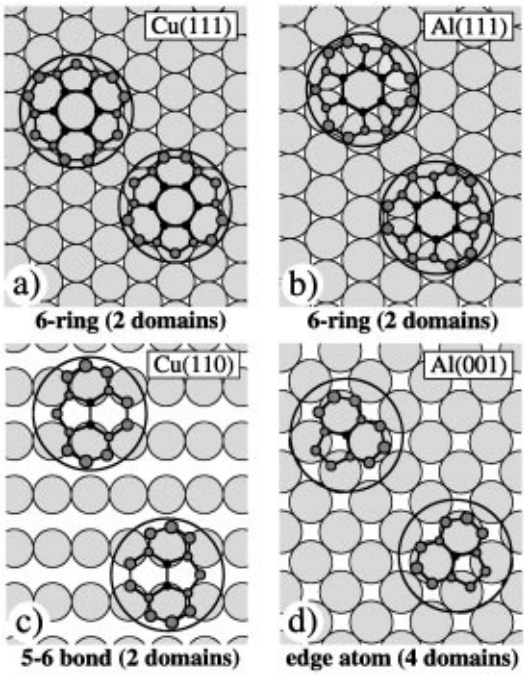

FIG. 4. Molecular orientations of C_{60} in monolayer films on (a) Cu(111), (b) Al(111), (c) Cu(110), and (d) Al(001) as determined from the XPD patterns shown in Fig. 2. The substrates are aligned as in Figs. 2 and 3. Substrate lattice spacings and C-C distances are properly scaled. For clarity, only the lower carbon atoms of the molecules are shown. The atoms closest to the substrate surface are shown as black dots. The approximate size of the molecules is indicated. The molecule-substrate registry and the intermolecular distances shown are arbitrary.

respectively (Fig. 4). The present results open the unique opportunity to correlate molecular orientation and electron/vibrational properties as obtained from other methods. We would like to point out that the application of XPD is by no means limited to the case of C_{60}: Higher fullerenes, coadsorption systems, endofullerenes, and nanotubes [6] are expected to be similarly well imaged by this technique. Off-center positions of metal atoms encapsulated into C_{60} molecules should be easily detectable by core-level XPD from the metal atom. Quenched or elongated molecules adsorbed on a surface are equally well suited candidates for an investigation by this technique.

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