

Doping-induced reorientation of C₆₀ molecules on Ag(111)

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X-ray photoelectron diffraction reveals that C₆₀ molecules adsorbed in a monolayer on Ag(111) take different orientations depending on the level of potassium doping. For half filling (K₃C₆₀) and complete filling (K₆C₆₀) of the lowest unoccupied molecular orbital, two distinct orientations are identified, exposing a hexagon or a 6-6 bond to the surface, respectively. For all the intermediate doping levels, the two orientations coexist, which is consistent with phase separation. Characteristic changes in the density of states, calculated for the two orientations within density functional theory, suggest intermolecular electron hopping as a driving force for the molecular reorientation.

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I. INTRODUCTION

Chemical doping is the most successful concept for tailoring the physical properties of solids, as exemplified in the physics of semiconductors, high-temperature superconductors, or alkali-metal doped fullerenes. While the typical role of a dopant is to provide extra charges to the host material, the resulting effects can be manifold. These effects should be properly understood in order to form a basis for intelligent materials design. This paper deals with a novel aspect of doping, unique to molecular crystals: we demonstrate that progressive filling of the conduction band in a two-dimensional (2D) C₆₀ crystal causes a reorientation of the elemental building blocks, which occurs without a detectable change in the crystal lattice.

C₆₀-based molecular crystals are of considerable interest because of their very rich electronic properties, including superconductivity with high critical temperature, ferromagnetism, and correlation-induced metal-insulator transitions with doping.^{1,2} This richness originates in the comparable magnitude of the electron-electron interaction, the electron-phonon interaction within the C₆₀ molecule, and the width of the conduction bands. Since a characteristic separation of energy scales is missing, many different degrees of freedom play an important role to determine the properties of the system, even when only one parameter changes. The effects of doping have been extensively studied. Changes in the electronic properties and in the vibrational modes were detected for solid C₆₀^{1,2} as well as for single layers adsorbed on metal surfaces.³⁻⁵ In bulk C₆₀ the role of the crystal structure has been invoked also: For high dopant densities, a structural change from fcc to bcc is observed between the superconducting K₃C₆₀ and the insulating K₄C₆₀ and K₆C₆₀ phases.^{6,7} It was also realized that the C₆₀ molecules order within the lattice. However, for a molecular crystal, the details of the bonding interactions are not completely understood. In 2D systems the interplay between bonding, electronic structure, and molecular orientation may be studied in more detail. Indeed, significant changes in the electronic structure of C₆₀ adsorbed in monolayer systems have been

attributed to different molecular orientations.^{8,9} The effects of doping on single isolated molecules have very recently been addressed by Yamachika *et al.*¹⁰ They can control the C₆₀ doping level by attaching K atoms with a scanning tunneling microscope tip, and they mention occasional rotations of the imaged molecule. By means of x-ray photoelectron diffraction (XPD) the orientation of C₆₀ can be directly determined with high accuracy.¹¹ Here we report a potassium-induced collective molecular reorientation within one monolayer of C₆₀ molecules adsorbed on Ag(111). In varying the concentration of potassium atoms, we find two different molecular orientations for K₃C₆₀ and K₆C₆₀ without observing changes in the translational symmetry of the C₆₀ overlayer. The molecular orientation in K₃C₆₀ is in line with the one based on density functional theory (DFT) calculations that reproduce the experimental band dispersion.¹² We evaluate the density of states for the two molecular orientations in the framework of DFT calculations, and discuss whether this drives the molecular reorientation.

II. EXPERIMENTAL

The experiments were performed in a VG ESCALAB 220 spectrometer modified with a computer-controlled two-axis sample goniometer.¹³ The XPD patterns were measured using Mg K α radiation with the sample kept at room temperature. Monolayer C₆₀ films were prepared by deposition of a multilayer and subsequent annealing of the sample to 300 °C. The quality of the C₆₀ layer and the coverage were checked by core-level photoemission and low-energy electron diffraction (LEED). Potassium was evaporated from a well-outgassed SAES getter source.

The lowest unoccupied molecular orbital (LUMO) doping level is calibrated according to the method proposed by Ceppek *et al.*⁴ When the valence band spectrum shows maximum intensity at the Fermi level, the band is half filled and there are three electrons in the LUMO; on the other hand, the C₆₀ LUMO is fully occupied by six electrons when the photoemission spectrum does not show further significant emis-

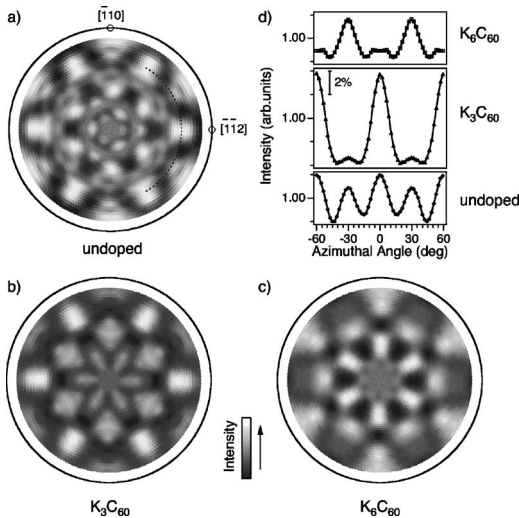


FIG. 1. Experimental C 1s XPD patterns ($E_{kin}=970$ eV) from potassium-doped C_{60} monolayers on Ag(111). (a), (b) and (c) Diffraction patterns measured at room temperature for three different LUMO doping levels: undoped, K_3C_{60} and K_6C_{60} , respectively. The orientation of the substrate as determined from the Ag $3d_{5/2}$ XPD pattern is also indicated. (d) Azimuthal photoelectron diffraction scans measured for the three doping levels at 70° polar emission angle along the dashed line in panel (a).

sion at the Fermi level, and we observe a saturation of the peak position with subsequent K exposure. In the following, we will refer to these two doping levels as K_3C_{60} and K_6C_{60} . In a monolayer system, this notation indicates only the filling of the C_{60} LUMO while it does not describe the alkali-metal stoichiometry of the layer. With these two points, that are independently determined, and supposing a linear relation between the K adsorption rate and the occupation of the LUMO, we find that 1.7 electrons are transferred from the Ag substrate to the molecules. Following a different calculation based on the integration of the LUMO intensity, the charge transfer is only 0.75 electrons per C_{60} .³ The possible reasons for these two different results are discussed in detail in Ref. 4. Both methods give significantly higher values than recent DFT calculations on the amount of electronic charge transfer.¹⁴

III. RESULTS AND DISCUSSION

One monolayer of C_{60} on Ag(111), prepared as described above, forms a $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure with one C_{60} per unit cell.¹⁵ The LEED patterns correspond to a hexagonal arrangement of molecules and we did not observe changes in the position of the diffraction spots upon doping with potassium. This indicates that the lattice of the C_{60} overlayer is not affected by the adsorption of the potassium atoms.

Figure 1 shows the experimental C 1s XPD patterns for three different doping levels: undoped, i.e., no potassium, K_3C_{60} , and K_6C_{60} . The data were measured in the forward scattering regime ($E_{kin}=970$ eV) and are presented as stereographic projections on a linear gray scale with maximum intensity corresponding to white. The patterns have been azi-

mutually averaged exploiting the rotational symmetry of the substrate and normalized to a smooth polar angle-dependent background typical for adsorbate emission. Prominent features appear at different polar and azimuthal emission angles in the three diffraction patterns. Since these patterns are directly related to the C_{60} orientation, this is clear evidence that the orientation of the molecules changes with doping. The azimuthal photoelectron diffraction scans measured at 70° polar emission angle illustrate the differences among the three structures [Fig. 1(d)]. In the undoped layer, we observe high photoemission intensity at 0° and $\pm 30^\circ$ with respect to the $[1\bar{1}2]$ azimuth; upon doping with potassium to K_3C_{60} , the intensity at 30° is significantly suppressed while at 0° it increases; for K_6C_{60} the azimuthal scan shows the opposite behavior. Up to now differences in the C_{60} XPD patterns have been observed on different high-symmetry single-crystal surfaces.^{11,16,17} These differences have been discussed in terms of molecule-molecule and molecule-substrate interactions. Here we show significant changes for different LUMO filling, where the observations indicate a collective reorientation of C_{60} molecules upon electron doping.

In order to understand the nature of this reorientation, we first solve the structure with an extensive R -factor analysis, i.e., comparing the experimental C 1s diffraction patterns to single-scattering cluster (SSC) calculations. Details on the C_{60} SSC calculations and the R -factor analysis can be found in Ref. 18. In the calculations we consider single molecular orientations on which the C_{60} symmetry of the substrate surface layer is imposed. In bulk C_{60} , it was observed that upon doping with potassium the molecules deform due to a weakening of the double bonds.^{19,20} The distortion does not exceed 0.02 Å in bond length and 0.5° in angle. Even though it can be expected that the effect is enhanced in a monolayer system, we can safely assume that it is too small to affect significantly the XPD pattern, and in our model we thus consider a rigid C_{60} cage. We find excellent agreement between theory and experiment for K_3C_{60} and K_6C_{60} , while for the undoped layer we do not even get a qualitative similarity of calculated and experimental patterns. The orientations that minimize the R factor for the two doped layers are shown in Fig. 2. The SSC patterns very well reproduce the overall positions and shapes of the prominent forward-focusing maxima in the experiments [Figs. 2(a) and 2(d)].²¹ When the LUMO is half filled, the C_{60} molecules face the Ag(111) surface with a hexagon, and when the LUMO is fully occupied, they face it with a bond between two hexagons (6-6 bond). These orientations of the molecular axes are similar to the ones known for the (111) layers of solid K_3C_{60} and K_6C_{60} .^{6,7} Moreover in both cases the minimum in the R factor indicates a significant azimuthal rotation of the molecules away from the high symmetry crystal axes (azimuthal misalignment) [Figs. 2(b) and 2(e)]. For K_3C_{60} this azimuthal rotation ($4 \pm 2^\circ$ with respect to the $[\bar{2}11]$ direction) is very close to the one known for bulk K_3C_{60} (7°).⁶ Density functional calculations on $K_3C_{60}/Ag(111)$ predict a similar orientation: In order to match the experimental band dispersion, Yang *et al.* propose an azimuthal misalignment of 10° . It is interesting to note that such a symmetry breaking has also been observed for C_{60} on Cu(110).¹⁶

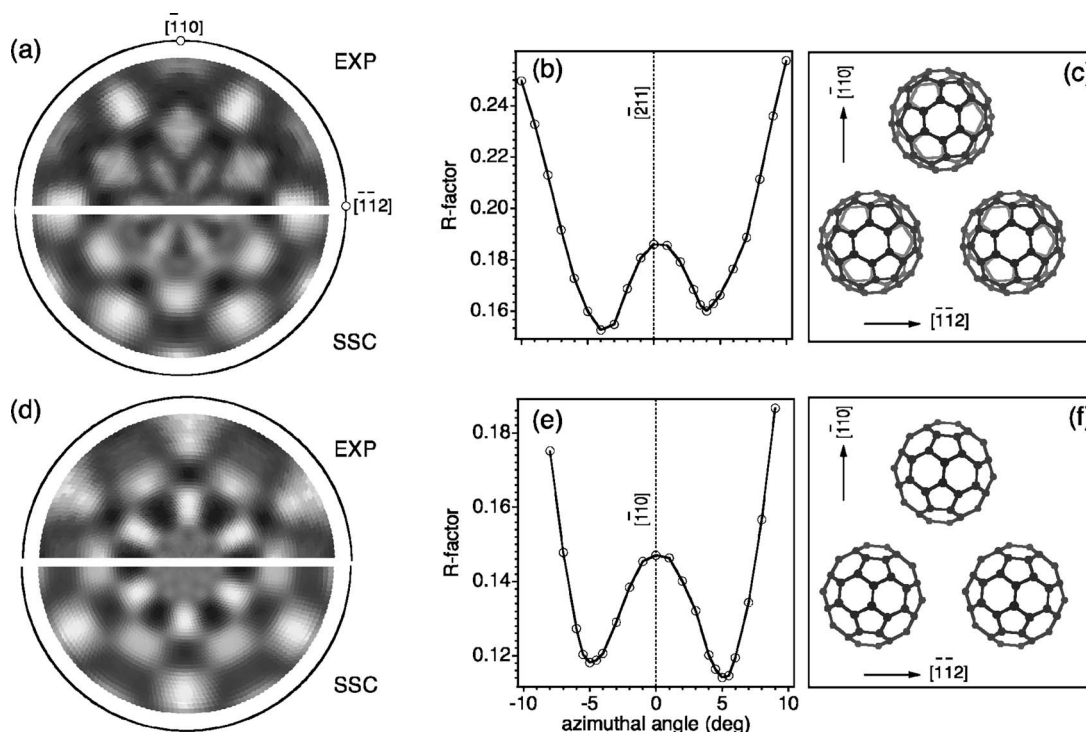


FIG. 2. Single-scattering cluster calculations reproducing the experimental XPD patterns. (a) and (d) K_3C_{60} and K_6C_{60} experimental (top) and SSC (bottom) patterns, respectively. (b) and (e) R factor as a function of an azimuthal rotation of the molecules away from the high-symmetry direction. For K_3C_{60} (K_6C_{60}) the minima correspond to an azimuthal rotation of 4° (6°) of the pentagon (bond between the hexagons) away from the $[\bar{2}11]$ ($[\bar{1}10]$) direction. (c) and (f) Top view of the molecular orientations, which minimize the R factor for K_3 and K_6C_{60} , respectively.

The orientation of the molecules in a potassium-doped monolayer is certainly related to a balance between molecule-molecule, molecule-ion, and molecule-substrate interactions. For example, calculations on single C_{60} molecules adsorbed on metal surfaces, where the hybridization between the C_{60} molecules is absent, show another orientation than experiments performed on full layers.²² The relative importance of the different interactions can be estimated from a comparison with bulk C_{60} . Since the orientations found in the monolayer are close to the ones known for the bulk systems, it seems that the molecule-molecule and the molecule-ion interactions are the dominant effects that determine the relative orientation in the layer. For the two orientations that we identified with XPD for K_3C_{60} and K_6C_{60} , it turns out that in both cases the molecules face each other through the pentagon rings. As discussed for bulk-doped C_{60} the LUMO density of states is highest on the pentagon rings.¹⁹ DFT calculations show that the LUMO bandwidth is extremely sensitive to the azimuthal orientation of the molecules.^{8,12} This indicates that the system arranges in order to maximize the intermolecular hopping rate of the electrons.

The fact that the single-orientation R factors do not reach low values for the undoped layer indicates that the molecules take more than one inequivalent orientation at low filling of the C_{60} LUMO. Figure 3 compares the XPD pattern of the undoped layer with a superposition of K_3C_{60} and K_6C_{60} with equal weight. The two patterns are very similar. In analogy with the results of the SSC calculations for K_3C_{60} and K_6C_{60} , this indicates that in the undoped layer, among all the pos-

sible orientations, the main contributions come from molecules sitting on the hexagon or on the bond between two hexagons, while at half and full filling of the LUMO one of these two configurations prevails. The coexistence of two orientations at low doping is a new aspect of the structure of a C_{60} monolayer on Ag(111). So far room-temperature scanning tunneling microscope (STM) experiments discussed either adsorption on a pentagon¹⁵ or on a hexagon ring.²³ DFT indicates that the latter is energetically favored while no calculations are available for the bond between two hexagons.¹⁴

In order to investigate how the molecular reorientation occurs and how many different phases we can identify, we measured the $C\ 1s$ core-level intensity as a function of the

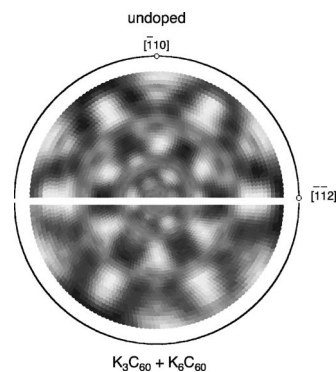


FIG. 3. $C\ 1s$ XPD pattern from the undoped C_{60} ML on Ag(111) (top) compared with a superposition of the experimental K_3C_{60} and K_6C_{60} patterns with equal weight (bottom).

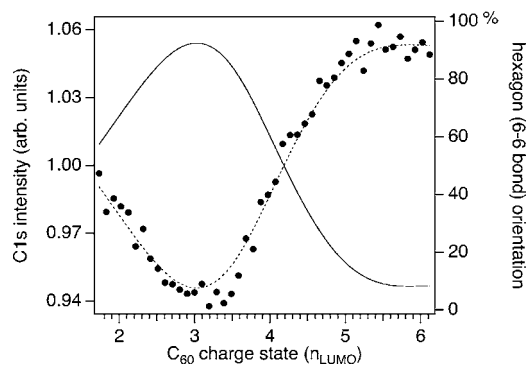


FIG. 4. C 1s photoemission intensity measured as a function of the filling of the C₆₀ LUMO (black circles). The right axis displays the percentage of molecules adsorbed on the hexagon (solid line) and on the bond between two hexagons (dashed line) as determined from a comparison between the experimental and the SSC intensities.

LUMO filling (Fig. 4). The spectra were recorded at normal emission while the C₆₀ layer was exposed to a constant flux of potassium atoms. The photoemission intensity changes significantly: It decreases from low doping levels up to half filling of the LUMO and it saturates to a maximum for a fully filled band. This behavior reflects the doping-induced reorientation and it is a photoelectron diffraction effect. The increase in intensity from half to full LUMO filling (12%) favorably compares with the relative change in intensity that we calculate for normal emission between a configuration where the molecules are adsorbed on the hexagon and a configuration with the molecules on the bond between two hexagons (15%). In particular, the linear behavior of the photoemission intensity from the minimum to the maximum supports the idea that no other orientational phases than the two shown for K₃C₆₀ and K₆C₆₀ characterize the layer. These results are compatible with phase separation between K₃ and K₆C₆₀, which is known for bulk C₆₀ and which has also been observed between the metallic and the insulating phase in a monolayer system.^{24,25}

The detailed mechanism for the molecular reorientation is not obvious: This effect may be due to the presence of the potassium ions or may be an electronic effect induced by the filling of the C₆₀ LUMO. To investigate the driving force of the transition, density functional theory calculations within the local density approximation (DFT-LDA) were performed in a plane-wave basis set.²⁶ Figure 5 shows the density of states in the highest occupied molecular orbital (HOMO)-LUMO energy range for the two experimental orientations of K₃C₆₀ and K₆C₆₀.²⁷ We model only a hexagonal, freestanding layer of C₆₀ molecules without potassium. The charge transfer from potassium is then considered within a rigid band model. This is a reasonable approximation around half filling since alkali atoms affect very little the LUMO band of K₃C₆₀.²⁸⁻³⁰ The differences in the LUMO density of states indicate that the orientation of the molecule influences significantly the DOS. Indeed remarkably different LUMO band

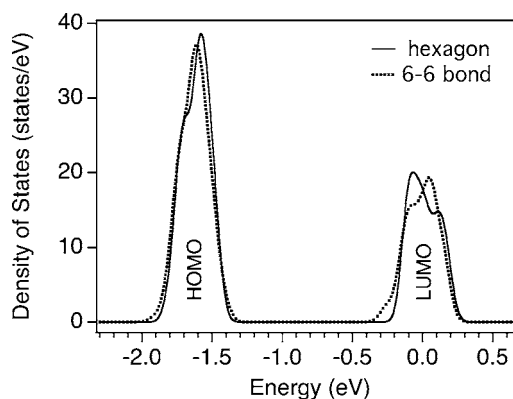


FIG. 5. DFT-LDA density of states of a hexagonal layer of C₆₀ molecules in the two different relative orientations of the molecule observed for K₃C₆₀ (hexagon) and K₆C₆₀ (6-6 bond). The distance between the molecules is set to the experimental value. The zero of energy is set to the Fermi energy at half filling of the LUMO.

structures are found for the two orientations. Interestingly, the changes in density of states are in line with the direction of the molecular reorientation: At more than half filling, the 6-6 bond orientation (K₆C₆₀) has a higher density of states at the Fermi level than the hexagon orientation (K₃C₆₀). Thus the system has to pay less energy for additional doping if it changes the orientation to the 6-6 bond. The total energies upon filling the LUMOs of the hexagon and the 6-6 bond orientation have been calculated: Energy differences of up to 20 meV/C₆₀ are found for the two orientations at the same doping level. These small values have to be considered in concert with the large adsorption energies and ionic potentials of the potassium atoms. Therefore, further experiments and calculations will be needed to definitively determine the relative importance of the alkali-metal point charges versus their contribution to the band filling on the molecular orientation.

IV. CONCLUSIONS

We have demonstrated that potassium induces significant structural changes in one monolayer of C₆₀ molecules adsorbed on Ag(111). While the lattice parameter of the layer remain constant, we can identify two different stable molecular orientations for K₃C₆₀ and K₆C₆₀. A DFT calculation, performed for both orientations, emphasizes the importance of the molecular orientation, in concert with the doping level, as a key parameter for the electronic properties of this class of low-dimensional materials.

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