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Metallization of the C60/Rh(100) interface revealed by valence photoelectron spectroscopy and density functional theory calculations

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The electronic structure of single and multiple layers of C60 molecules deposited on a Rh(100) surface is investigated by means of valence photoemission spectroscopy and density functional theory calculations. The binding of the fullerene monolayer to the metal surface yields the appearance of a new state in the valence band spectrum crossing the Fermi level. Insight into the metallization of the metal/fullerene interface is provided by the calculated electronic structure that allows us to correlate the measured interface state with a strong hybridization between the Rh metal and the C60 lowest unoccupied molecular orbital (LUMO), resulting in a net charge transfer from the Rh metal to the C60 lowest unoccupied molecular orbital (LUMO). This results in a net charge transfer of ≈0.5e–0.6e from the metal to the p states of the interfacial C atoms. The charge transfer is shown to be very short range, involving only the C atoms bound to the metal. The electronic structure of the second C60 layer is already insulating and resembles the one measured for C60 multilayers supported by the same substrate or calculated for fullerenes isolated in vacuum. The discussion of the results in the context of other C60/metal systems highlights the distinctive electronic properties of the molecule/metal interface determined by the Rh support. © 2010 American Institute of Physics. [doi:10.1063/1.3432778]

I. INTRODUCTION

An important scientific challenge in carbon-based materials is the metallization of fullerene layers upon electron doping. It is well known that C60 is a strong electron acceptor, and electron doping of C60 solids is easily achieved, for example, by intercalation of alkali metals.1–3 Electron-doped intercalated C60 compounds show several phases with distinct properties, among which the most interesting are the metallic and superconducting phases with an excess charge of almost 3 electrons/molecule.1–10

The intercalation of dopant atoms is not the only way to form metallic C60 systems. The chemisorption of a single layer of C60 on metal surfaces, which typically involves hybridization between the molecular orbitals of C60 and the metal states near the Fermi level as well as interface charge reorganization, may result in a net charge transfer from the metal to the C60 lowest unoccupied molecular orbital (LUMO).11–18 This mechanism is known to drive the chemisorbed molecular layer into a metallic state only for Cu, Ag, and Au metal surfaces,11,12,15,16,18,19 while for all the other metallic surfaces investigated so far,13,14,17,20–24 the metallic character of the overlayer is not clearly proved. This behavior is mainly governed by molecule-substrate interfacial interactions or by specific electronic properties of the substrate. Yet, other noble metal surfaces such as Rh (Refs. 20 and 21) and Pt (Refs. 19 and 22) should give a clear metallic character to the C60 overlayer, but the reported experimental evidence seems to exclude these substrates19,22 or does not provide a clear conclusion.20,21

For Rh, in particular, the observed changes in the work function upon chemisorption of 1 ML of C60 on Rh(111)20,21 suggested that the hybridization of Rh d-states with the highest occupied molecular orbital (HOMO) is more effective than the hybridization with the LUMO, resulting in a net delocalization of electrons from C60 to the Rh surface. However, no new photoemission states were observed near the Fermi level, while the presence of a transition was reported in the electron energy loss spectra, suggesting indeed that some electrons were instead populating the LUMO (t1u) orbitals.21

In the present work, we investigate, by means of valence band photoemission spectroscopy and density functional theory (DFT) calculations, the electronic structure of C60 molecules deposited onto a Rh(100) surface. The valence band spectra show the appearance of a new state at the Fermi level, which calculations reveal to be a hybrid Rh–C60 state. This state has a significant component over the molecular LUMO state, resulting in a net charge transfer from the Rh substrate to C60 and giving a metallic character to the C60 monolayer.

This paper is organized as follows: the details of the calculations or by specific electronic properties of the substrate. Yet, other noble metal surfaces such as Rh (Refs. 20 and 21) and Pt (Refs. 19 and 22) should give a clear metallic character to the C60 overlayer, but the reported experimental evidence seems to exclude these substrates19,22 or does not provide a clear conclusion.20,21

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photoemission measurements and of the DFT calculations are described in Sec. II. Our results are then reported and discussed in Sec. III by considering first a single monolayer of C$_{60}$ adsorbed on Rh(100) (Sec. III A) and then a molecular bilayer on the same metal surface (Sec. III B). The main findings are finally summarized in Sec. IV.

II. METHODS

A. Experimental measurements

The measurements were performed in the ultrahigh vacuum experimental chamber (base pressure of about $10^{-10}$ mbar) of the SuperESCA beamline at the Elettra Synchrotron. Valence band photoemission data were recorded with a double-pass hemispherical electron energy analyzer at normal emission using photon energies of 140 and 70 eV with an overall energy resolution of about 80 meV. The binding energy values are defined with respect to the Fermi level ($E_F$) of the clean Rh(100) substrate. The Rh(100) substrate was cleaned by cycles of Ar$^+$ sputtering and high temperature annealing in oxygen and hydrogen atmosphere. C$_{60}$ was evaporated from a degassed tantalum crucible and deposited on the clean rhodium substrate kept at 400 K to form the multilayer. The thickness of the multilayer was 10 $\pm$ 1 ML. The formation of the monolayer is carried out either by thermal desorption (TD) of the deposited multilayer by annealing the film above 550 K or by depositing C$_{60}$ with the substrate kept at 600 K. Here we used both techniques. The formation of a second layer above the monolayer was obtained by TD of the multilayer following the C 1s core level (Fig. 1) or by depositing another layer above the monolayer. In both cases, we know that we have not formed the third layer (because the core level is shifted and the valence band is insulating like the multilayer) and that the amount of C$_{60}$ is more than 1.5 ML (see Fig. 1).

FIG. 1. C 1s core level spectra obtained during TD of a C$_{60}$ multilayer. Some selected spectra are reported.

B. Numerical simulations

DFT calculations were performed with the Perdew–Burke–Ernzerhof exchange-correlation functional in a plane-wave pseudopotential framework, as implemented in the VosCF code of the QUANTUM ESPRESSO distribution, using ultrasoft pseudopotentials. The C$_{60}$ monolayer adsorbed on the Rh(100) surface was simulated in a $c(4 \times 6)$ periodic arrangement (see dashed lines in Fig. 2) by using the supercell displayed in Fig. 2 (solid lines). In the absence of low energy electron diffraction (LEED) data for this specific system, we modeled a coherent interface between the squared lattice of the Rh(100) surface and a monolayer of C$_{60}$ molecules in a hexagonal arrangement (slightly distorted to yield commensurability). The periodicity was set such that the average C$_{60}$–C$_{60}$ intermolecular distance (10.4 Å) was as close as possible to the corresponding experimental value in the hexagonal C$_{60}$ arrangement along the (111) planes of a fcc fullerene crystal (10.1 Å). We stress, however, that due to the weakness of intermolecular interactions, the main conclusions of our study do not depend on this specific periodicity of the model structure. Three- and four-layer Rh slabs were used as simplified models for the Rh(100) surface with the calculated equilibrium bulk lattice parameter of 3.85 Å. In the resulting distorted hexagonal symmetry of the monolayer, the shorter distances between two neighboring C$_{60}$ molecules are 9.81 and 10.92 Å. Opposite surfaces of adjacent supporting metal slabs were separated by more than 16.5 Å, leaving more than 8 Å between the top of the adsorbed C$_{60}$ molecule and the periodic image of the metal surface above it. Brillouin zone integrations for metallic structures were performed on a $(4 \times 4)$ Monkhorst–Pack grid consisting of 10 points (including $\Gamma$) and with a Methfessel–Paxton smearing of 0.01 Ry. Isolated fullerene molecules were simulated by sampling electronic states only at the $\Gamma$ point. In the case of the adsorbed monolayer, all atomic positions were relaxed according to the Hellmann–Feynman forces, except for the two lowermost Rh layers whose distance was kept fixed to the bulk value. In addition to a single layer of C$_{60}$ molecules, the effects of a second layer were also investigated. In this case, the C$_{60}$ molecules on the top layer were arranged above hollow sites left between the arrangements of C$_{60}$ molecules on the bottom layer, with one of the hexagons facing downward. A
vertical distance of 1.5 Å was set between the two layers. In this case, the vacuum region between the topmost atoms of the second-layer C₆₀ molecules and the bottom of the next Rh surface slab was increased to 12 Å. No further structural relaxation was performed for the bilayer system.

III. RESULTS AND DISCUSSION

A. C₆₀ monolayer on Rh(100)

1. Photoemission data: Interface electronic states

Figure 3 shows the valence band photoemission spectra of (a) 1 ML of C₆₀ on Rh(100), (b) a clean Rh(100) surface (reduced by a factor of 4.5, see text for details) and (d) a C₆₀ multilayer. The spectrum (c) is obtained by the difference between spectra (a) and (b). All these spectra are measured with a photon energy of 140 eV. Inset: the same spectra described above obtained with a photon energy of 70 eV. Here, an attenuation factor of 6.0 (see text for details) was used for the spectra difference (c).

The difference spectrum displayed in Fig. 3(c) clearly shows the peaks due to the HOMO and HOMO−1 states, which are broadened with respect to the corresponding ones in the multilayer case. Similar broadening and splitting of the HOMO states was observed on the monolayer adsorbed on Al surfaces and Ge(111), where the molecular bonding is expected to be mainly covalent. On these surfaces, the C₆₀ monolayer is insulating. In the case of Rh(100), additional features are present between the HOMO and EF, where a new sharp peak appears. In order to confirm that this peak at EF is not an artifact of the experimental setup (for example, resulting from a misalignment of the spectra due to instabilities of the photon energy beam), we show in the inset of Fig. 3 the same spectra measured with a different photon energy, i.e., 70 eV. In this case, the attenuation factor of the clean Rh(100) has been chosen to be 6, which corresponds to the assumption of an inelastic mean free path for photoelectrons of 4.8 Å. One can see that the peak at the Fermi level is visible also in this case and the other peaks are the same as obtained at 140 eV. We note that in this case the C₆₀ features are suppressed because of the increased weight of the Rh character in the hybrid states due to reasons related to photoemission cross section. This indicates that the C₆₀ and Rh states are strongly hybridized, in particular, for binding energies between EF and 5 eV, where the Rh d bands superimpose to the HOMO and HOMO−1 states. Since the Rh d bands are known to extend a few eV above EF, similar hybridization is also expected for the LUMO and LUMO+1 C₆₀ orbitals.

The new feature at EF may have different origins. The increase in the peak intensity reducing the photon energy indicates that the interface state at EF has a strong Rh contribution due to cross section effects and we cannot exclude the possibility that this feature originates exclusively from Rh states without any molecular contribution (in this case, the C₆₀ monolayer would be an insulator). According to this interpretation, the C₆₀ overlayer would simply act as a momentum scatterer for the Rh photoemitted electrons, averaging the states inside the Brillouin zone. This scenario would then lead to an increase in the density of states (DOS) at EF in the Γ point, hence compatible with our spectra at normal emission. Instead, the electronic structure calculations described in the following support another interpretation. They provide evidence that the peak at the Fermi level originates from a charge transfer from the metal to the molecular states, leading to a metallization of the interface.
2. DFT calculations: Geometry optimization and energetics of adsorption

The equilibrium adsorption geometry was determined by a two step procedure. We first performed a series of single point total-energy calculations without geometric optimization in which C$_{60}$ was positioned at a vertical height of 2 Å above the metal surface. The energy landscape was explored as a function of molecular lateral translations and rotations. In particular, we explored the high-symmetry configurations obtained by placing the molecule on the metal substrate with one of its hexagon, pentagon, or hexagon-pentagon edge facing either the hollow, top, or bridge sites of the Rh(100) square lattice. In addition, for each of these configurations, we also considered rotations of the molecule around its axis perpendicular to the surface through a series of high-symmetry angles. The lowest-energy structure was then fully relaxed. During the structural optimization, the molecule approached the surface decreasing the vertical distance to 1.7 Å (calculated between the center of the closest C atom and the interfacial Rh atom).

The resulting lowest-energy adsorption geometry is displayed in Fig. 4. In this configuration, a pentagon-hexagon edge of C$_{60}$ is oriented parallel to one of the [001] directions of the Rh surface and is in the middle of a square surface, on top of a second-layer Rh atom. The relevant C–Rh bond lengths are displayed in Fig. 4(a), where the interfacial hexagon and pentagon of the fullerene are highlighted by dashed yellow lines and the six C atoms bound to the metal surface are marked by yellow circles. The Rh atoms close to the contact area display very small displacements ≤0.1 Å with respect to the equilibrium positions, while the position of the remaining metal atoms is unaffected by C$_{60}$ adsorption.

The molecule/metal distance predicted by the DFT calculations (1.7 Å) is much shorter than the corresponding distance obtained for the adsorption of C$_{60}$ on other transition metal surfaces: 2.4 Å for C$_{60}$/Ag(111), 2.5 Å for C$_{60}$/Au(111), or 2.5 Å for C$_{60}$/Ag(100) (estimated from Fig. 6 of Ref. 35). The latter comparison indicates that the short molecule-metal distance in the present C$_{60}$/Rh(100) system is not a result of the specific geometry of the (100) surface but is due to the nature of the Rh metal, in particular, the low value of the work function and the extension of the d band across the HOMO and LUMO. In order to give further evidence to this fact, we have performed a parallel study on a C$_{60}$ monolayer adsorbed on a Au(100) surface, whose d band is ≈2 eV below the LUMO. In this case, we obtained a much larger distance of 2.8 Å, compatible with the value reported for the Au(111) surface.

The short molecule/metal distance in the C$_{60}$/Rh(100) system results in a strong metal-molecule interaction, in analogy with the C$_{60}$/Rh(111) case$^{20,21}$ and actually observed here using TD spectroscopy (results not shown$^{36}$). Indeed, a large adsorption energy of 3.62 eV/molecule is estimated from the total energy difference defined as $E_{C_{60}/Rh(100)} - (E_{C_{60}} + E_{Rh(100)})$, where $E_{C_{60}/Rh(100)}$, $E_{C_{60}}$, and $E_{Rh(100)}$ are the total energies of the C$_{60}$ monolayer adsorbed on the Rh(100) surface, the C$_{60}$ monolayer isolated in vacuum, and the Rh(100) clean surface, respectively, calculated in the same simulation supercell.

3. DFT calculations: Electronic structure and interface metallization

The total DOS for a single C$_{60}$ monolayer adsorbed on Rh(100) is shown in Fig. 5 (solid black line in the upper panel) together with its decomposition into partial contributions from the Rh and C atoms (displayed in Fig. 5 as gray and red areas, respectively). The latter was obtained by projecting the self-consistent DOS onto the corresponding atomic orbitals (PDOS denotes projected DOS). For reference, the energy of the molecular states for an isolated fullerene molecule is also shown in the lower panel of Fig. 5 (blue areas). Energies are referred to the Fermi energy of the C$_{60}$/Rh(100) system, while, in order to facilitate the fingerprinting of the peaks, the energies of the molecular states for the isolated fullerene are shifted so as to align with the corresponding ones in the C$_{60}$/Rh(100) system. We remark that the calculated HOMO and LUMO gap of the C$_{60}$ is under-
estimated by 0.7–0.8 eV, in agreement with previous DFT calculations performed with a similar functional.\textsuperscript{37,38}

The comparison between the Carbon PDOS of the isolated (blue area in Fig. 5) and supported (red area) fullerences shows that the interaction with the metal surface strongly modifies the occupied HOMO and HOMO−1 as well as the LUMO and LUMO+1, while the remaining states are weakly perturbed upon adsorption. The position of the Fermi energy is pinned by the metallic surface and falls within the Rh $d$ band (gray area). The C-PDOS of the supported $C_{60}$ monolayer (red area) clearly shows the presence of a continuum of states between the HOMO and LUMO, with a clear peak at $E_F$ as observed in the experimental spectra, hence proving the metallization of the metal/molecule interface. The corresponding molecular states are shown in Fig. 6. These states are strongly hybridized with the underlying Rh metal states and can be directly correlated with the strong molecular binding to the metal surface discussed above.

The formation of interfacial Rh–C bonds results from a transfer of charge from the Rh surface to the interfacial C atoms of the fullerene. A Löwdin charge analysis\textsuperscript{39} shows that with respect to a gas phase fullerene, there is a substantial increase in the charge only on the six C atoms that are bound to the Rh surface: +0.10$e$ on the two atoms forming the edge between the interfacial hexagon and pentagon, +0.09$e$ on the two atoms of the hexagon, and +0.07$e$ on the two atoms of the pentagon. Variations in the Löwdin charge on all other C atoms are smaller than 0.02$e$. Overall, a charge transfer of $\approx 0.6e$ can be estimated from differences in the Löwdin charges of the C and Rh atoms with respect to the corresponding values in the isolated $C_{60}$ molecules and clean Rh(100) surfaces.

The electron density difference and the differential charge density integrated in the $xy$ planes parallel to the interface are displayed in Fig. 6. Positive/negative values (red/blue areas) indicate charge accumulation/depletion. The charge difference is calculated with respect to the sum of the electron distributions of the isolated 1ML $C_{60}$ system and of the Rh(100) metal slab. Horizontal lines indicate the positions of the metal slab and of the fullerene. This analysis provides further evidence of the charge transfer from the metal to the interfacial C atoms, showing that this charge transfer process involves mostly the atoms in the contact region, with a minor contribution from the second layers of Rh and C atoms. An alternative measure of the total charge transfer from the metal to the molecule can be obtained by evaluating the integral highlighted by the gray area in Fig. 6, resulting in 0.5$e$.

### B. $C_{60}$ bilayer on Rh(100)

The analysis of a double layer system allows us to prove the metallization of the fullerene/Rh interface also in the presence of thicker molecular multilayers. As in other metallic systems, we demonstrate that the $C_{60}/$Rh(100) interface mainly affects the electronic properties of the first layer only. The valence photoemission spectrum of 2 ML $C_{60}$/Rh(100) is shown in Fig. 7 (black solid line). By considering the attenuation factor of the signal due to the electron escape depth,\textsuperscript{32} the contribution from the first layer should be reduced by a factor of $\approx 6$ with respect to the one of the outermost molecules, while the signal from the Rh substrate should be attenuated by a factor of $\approx 36$ and therefore almost negligible. Indeed, the spectrum coming from the bilayer system shows a small spectral intensity at $E_F$, which, according to Fig. 7, is due to the attenuated emission of the first $C_{60}$ layer. The first layer is therefore confirmed to be metallic independent of the presence of other fullerences above it. Given the high attenuation factor, the metallic signal from the metal/molecule interface is already lost with increasing
number of layers. The subtraction reported in Fig. 7 indicates that the spectrum of the second C$_{60}$ layer is insulating like the multilayer spectrum.

In agreement with the experimental findings, our DFT calculations indicate that C$_{60}$ layers in a multilayer arrangement adsorbed on the Rh(100) surface display an insulating behavior starting from the second layer. The PDOS projected over carbon atoms of the first and the second C$_{60}$ layers are displayed in Fig. 8, together with the reference molecular states for an isolated fullerene molecule (blue area). The Fermi level of the bilayer system is pinned by the charge transfer at the C$_{60}$/metal interface of the first layer, which displays the same metallic character and charge transfer behavior discussed for the monolayer case. As discussed above, we notice that even though the first monolayer displays a metallic character, the PDOS of the second layer is already insulating and its PDOS shows the characteristic HOMO-LUMO gap of the isolated C$_{60}$ molecule. This analysis clearly demonstrates the short-range character of the surface effects on the deposited C$_{60}$ layers.

IV. CONCLUSIONS

This work emphasizes the role of molecular charge transfer in the ground state of the electronic structure of 1 ML of C$_{60}$ on Rh(100), a case of mainly covalent bonding similar to the Al surfaces. The metallization of the system obtained by adsorbing C$_{60}$ molecules on the Rh(100) surface is demonstrated by valence photoemission experiments combined with DFT calculations. The measured spectra for the 1 ML case show the presence of a new peak crossing the Fermi level. The analysis of the calculated electronic structure reveals that the metallic nature of the system is due to a charge transfer of $\approx 0.5e - 0.6e$ from the metal to the $p$ states of the interfacial C atoms, which are strongly hybridized with the underlying Rh atoms. This yields to a metal-molecule distance and to a calculated binding energy of 1.7 Å and 3.4 eV, respectively. The characteristic strong bonding of fullerenes to the Rh metal surface is evident by comparing these values to other C$_{60}$/metal systems. We note that, from our calculations, this strong bonding is achieved in the absence of surface reconstructions or defects below the adsorbed fullerene, which are typically essential for the chemisorption of C$_{60}$ on other noble metals, such as Au (Ref. 41) or Pt. 42

The analysis of a bilayer system in which 2 ML of C$_{60}$ were adsorbed on the Rh(100) surface allow us to conclude that the same metallization discussed above involves only the first molecular layer. Both the experimental and theoretical analysis shows that the electronic structure of the second layer is already insulating and weakly perturbed with respect to the spectra of the metal-supported C$_{60}$ multilayers.

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