Electronic structure of C_{60} on Au(887)

F. Schiller,^{a)} M. Ruiz-Osés, and J. E. Ortega

Donostia International Physics Center, Paseo Manuel Lardizabal 4, E-20018 Donostia-San Sebastián, Spain; Departamento de Física Aplicada I, Universidad del País Vasco, Plaza de Oñate 2, E-20018 Donostia-San Sebastián, Spain; and Centro Mixto CSIC/UPV, Paseo Manuel Lardizabal 4, E-20018 Donostia-San Sebastián, Spain

P. Segovia and J. Martínez-Blanco

Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain and Instituto Universitario de Ciencia de Materiales "Nicolás Cabrera," Universidad Autónoma de Madrid, E-28049 Madrid, Spain

B. P. Doyle

Laboratorio Nazionale TASC, INFN-CNR, ss. 14, km 163.5, Area Science Park, I-34012 Basovizza, Trieste, Italy

V. Pérez-Dieste and J. Lobo

Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen, Switzerland

N. Néel, R. Berndt, and J. Kröger

Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität, D-24098 Kiel, Germany

(Received 23 March 2006; accepted 16 August 2006; published online 13 October 2006)

We present an analysis of the electronic structure of C_{60} adsorbed on a vicinal Au(111) surface at different fullerene coverages using photoemission, x-ray absorption, and scanning tunneling microscopy/spectroscopy (STS). STS provides a straightforward determination of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels with respect to the Fermi energy. At C_{60} coverages of 0.5 and 1 ML a 2.7 eV wide HOMO-LUMO gap is found. The near-edge x-ray absorption fine structure (NEXAFS) spectrum for the 0.5 ML C_{60} nanomesh structure displays a significant intensity at the low energy side of the LUMO exciton peak, which is explained as due to absorption into HOMO-LUMO gap states localized at individual C_{60} cluster edges. From 0.5 to 1 ML we observe a rigid shift of the HOMO-LUMO peaks in the STS spectra and an almost complete quenching of the gap states feature in NEXAFS. © 2006 American Institute of Physics. [DOI: [10.1063/1.2354082](https://doi.org/10.1063/1.2354082)]

I. INTRODUCTION

Self-organization of molecules attracts increasing attention in nanoscience and nanotechnology due to its potential in mass fabrication of identical nanoscale structures for miniature devices.¹ Prepatterned substrates, such as vicinal surfaces, give rise to ordered structures in large single domains, can induce chirality, or can force different supramolecular bonding geometries.^{2,3} The successful use of vicinal surfaces as templates to fabricate well-ordered structures was shown in the past, e.g., self-organization of Fe (Ref. 4) or Dy (Ref. 5) nanowires on stepped Si surfaces and two-dimensional long-range-ordered growth of Co islands on vicinal Au(111).⁶ Recently a low-temperature scanning tunneling microscopy (STM) study reported a regular pattern of self-organized C_{60} islands on Au(887) with 0.5 ML coverage, which reflects on a large lateral scale the two-dimensional periodicity of Au(887).⁷

C_{60} belongs to the group of fullerenes and presents one of the simplest molecular structures.⁸ Since the discovery of superconductivity in alkali-metal- C_{60} compounds,^{9,10} which

is closely related to the electron transfer from the substrate,^{11,12} much attention has been paid to C_{60} adsorption on metallic surfaces. The C_{60} monolayer is particularly interesting due to the reduced gap width between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The HOMO-LUMO gap has been probed using different spectroscopic techniques, such as optical absorption, or directly measured by scanning tunneling spectroscopy (STS) or by a combined photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES) experiment. For the latter, one can observe a large variation from $\Delta E=4.9$ eV for C_{60} in the gas phase down to $\Delta E=3.3$ eV in thick films on Ag(111) (Ref. 13) or Au(111),¹⁴ and to $\Delta E=2.2$ eV for C_{60} monolayers on Ag(111).¹³ Such variation is not related to changes in the structure of molecular levels, but is rather due to characteristic many-body final state effects in photoemission.^{13,15} For future electronic device fabrication the conductivity of the surface as well as the surface-molecule charge transfer are also interesting issues. The latter has been claimed to be negligible in C_{60} on Au(111) (Ref. 16) or Pt(111),¹⁷ in contrast to approximately two electrons transferred in Cu(111).¹⁸ On the other hand, as deduced from the peak observed at the Fermi energy in pho-

^{a)}Electronic mail: schiller@sc.ehu.es

FIG. 1. (a) Constant-current image of clean Au(887) ($62 \times 62 \text{ nm}^2$, 120 mV, 1 nA). Inset: Processed close-up view to reveal the discommensuration lines running along the $[\bar{2}11]$ direction ($14 \times 14 \text{ nm}^2$, 80 mV, 1 nA). (b) Constant-current STM image of $\text{C}_{60}/\text{Au}(887)$ at 0.1 ML ($62 \times 62 \text{ nm}^2$, 745 mV, 0.1 nA). (c) Constant-current STM image of $\text{C}_{60}/\text{Au}(887)$ at 0.5 ML ($290 \times 290 \text{ nm}^2$, 745 mV, 0.1 nA).

toemission spectra, the LUMO of the C_{60} monolayer on Cu(111) (Ref. 18) and Ag(111) (Ref. 19) is partially occupied. On Au(111) the photoemission spectra for the C_{60} monolayer also show a similar, upward dispersing Fermi feature, from which a significant transfer of 0.8 electron per C_{60} from the Au substrate is deduced.²⁰ Such charge transfer disagrees with STS data that show LUMO features at least 0.6 eV away from the Fermi edge^{16,21,22} and also to theoretical works that predict a negligible charge transfer.¹⁶ Therefore the metallic character of the C_{60} monolayer on Au(111) is not clear yet.

In this paper we investigate the electronic structure of C_{60} adsorbed on a vicinal Au(111) surface by STS, PES, and near-edge x-ray absorption fine structure (NEXAFS) measurements. The STS spectra show HOMO and LUMO peaks, which define the same HOMO-LUMO gap $\Delta E = 2.7 \text{ eV}$ for both the 0.5 ML nanomesh and the close-packed monolayer. Nonetheless, HOMO and LUMO peaks are observed to shift uniformly, suggesting charge transfer and changes in the dipole layer at the interface from 0.5 to 1 ML. With NEXAFS we have been able to observe the presence of a significant density of electronic states that fill up the HOMO-LUMO gap at 0.5 ML coverage and disappear in films thicker than 1 ML. Such gap states, which are not detected in STS, appear as characteristic of finite size, two-dimensional C_{60} islands and clusters, becoming the specific electronic state feature of the highly ordered C_{60} clusters on Au(887).

II. EXPERIMENTAL DETAILS

STM experiments were carried out with a homebuilt low-temperature scanning tunneling microscope.⁷ Photoemission and absorption (total yield) were performed at beam lines SIS-HRPES and BEAR of the synchrotron radiation facility SLS in Villigen (Switzerland) and Elettra in Trieste (Italy), respectively. We used linearly polarized light (100% and approximately 90% in Villigen and Trieste, respectively) with 45° incidence and normal emission conditions. The Au(887) single crystal was cleaned by various cycles of argon ion sputtering (800 V, 15 min) and annealing

(700 K, 15 min) until the characteristic low energy electron diffraction (LEED) pattern was observed. This consists of a square pattern around the hexagonal crystal spots, i.e., a sharp splitting due to the step lattice and the extra splitting due to the periodic discommensuration lines separating hexagonal-close-packed (hcp) from face-centered cubic (fcc) stacking domains, which run nearly perpendicular across the step edges. C_{60} molecules were evaporated from a resistively heated tantalum crucible keeping the pressure below 10^{-7} Pa . The deposition was carried out with the sample held at 300 K in order to allow the C_{60} molecules to diffuse on the surface. Then, the sample was cooled down slowly to 9 K in the case of the STM experiment, to 150 K in the case of the PES/NEXAFS. The base pressure during the experiment was in the low 10^{-9} Pa (STM)– 10^{-8} Pa (PES and NEXAFS) range.

In the STM experiment the coverage was calculated directly from constant-current STM images and compared with the LEED pattern (1 ML corresponds to a density of C_{60} molecules of 1.2 nm^{-2}). The latter was used to calibrate the C_{60} coverage in synchrotron experiments, together with valence band and core-level photoemission analysis. To cross-check the calibration, a multilayer film was deposited and slowly heated to 650 K, in order to produce a monolayer.²⁰ The corresponding C 1s core level and the valence band photoemission spectra were used as the reference to calibrate submonolayer signals.

III. RESULTS AND DISCUSSION

A. STS: HOMO-LUMO gap

The Au(887) surface is vicinal to the (111) plane with a 3.5° tilt angle towards the $[\bar{2}11]$ direction, resulting in a 3.9 nm step distance. It contains step edges running along the $[0\bar{1}1]$ direction with a surface reconstruction that separates areas of hcp and fcc regions.²³ Figure 1(a) shows the constant-current STM images of the clean Au(887) surface. The inset contains a close-up view, which has been processed to reveal the surface reconstruction of Au(887). The bright

FIG. 2. Spectra of the differential conductivity dI/dV for 0.5 ML (lower spectrum) and 1.0 ML (upper spectrum). The upper spectrum was offset by 1 nS. For the lower (upper) spectrum the tunneling barrier was set at -3 V and 0.1 nA ($+3$ V and 0.1 nA). The full lines represent fits to the experimental data (depicted as dots).

areas mark discommensuration lines between the fcc and hcp regions. The periodicity along the steps is 7.2 nm with the fcc area being wider than the hcp one. The C₆₀ adsorption process is strongly selective. The low coverage image in Fig. 1(b) reveals that C₆₀ molecules primarily adsorb at step edges of fcc areas, forming four to five molecule long chains in fully decorated fcc steps.⁷ The molecules adsorb at the upper terrace and are imaged as circularly shaped white protrusions. Increasing the exposure of C₆₀ leads to a further occupation of the fcc sites: fullerene chains are added leading to rectangularly shaped islands, most containing four C₆₀ chains at a coverage of 0.5 ML. Each island comprises a step edge of the substrate. The islands are clearly separated from each other by surrounding substrate material (unoccupied hcp and fcc domains). The resulting superstructure is a highly ordered pattern of rectangular C₆₀ islands [see Fig. 1(c)], which reflects the periodicity of the Au(887) sample.⁷ Further adsorption leads to a completely covered Au(887) surface with the C₆₀ film revealing hexagonal order. The LEED pattern corresponding to the complete monolayer presents, as in the case of the C₆₀ monolayer on a Au(111) substrate, a sharp $2\sqrt{3} \times 2\sqrt{3}R30^\circ$ reconstruction.

In Fig. 2 we present spectra of the differential conductivity (dI/dV) as a function of the sample voltage. Occupied (unoccupied) states are located at negative (positive) voltages. The spectra were measured with the tip placed upon the center of C₆₀ molecules for coverages of 0.5 ML (lower spectrum) and 1.0 ML (upper spectrum). Both spectra are the average over single spectra acquired on a multitude of molecules and using a variety of tips. Note that the upper spectrum has been offset by 1 nS for clarity. For positive voltages we associate the peaks below 1 eV and above 2 eV to the spectroscopic signature of the LUMO and the second-to-lowest unoccupied molecular orbital (LUMO+1), respectively. At 0.5 ML we observe further a weak shoulder at ≈ -2 eV, which turns into a more pronounced feature at 1.0

TABLE I. Energy positions of molecular orbitals of C₆₀ on Au(887) as derived from Ref. 16 (single molecules) and from fits to the tunneling spectroscopy data presented in Fig. 2.

Coverage	HOMO (eV)	LUMO (eV)	LUMO+1 (eV)
Single molecule	-1.7 ± 0.2	1.0 ± 0.2	2.2 ± 0.2
0.5 ML	-1.77 ± 0.02	0.91 ± 0.01	2.15 ± 0.01
1.0 ML	-1.89 ± 0.02	0.82 ± 0.01	2.02 ± 0.01

ML. We attribute these spectral weights to the HOMO of C₆₀. These assignments are not based on calculations but on a comparison with the results of STM/STS experiments for C₆₀ on Ag(100) and Au(111),^{16,24} where the energetic positions of the molecular orbitals are similar. In order to find the peak positions we fitted the spectra by a superposition of five Gaussians and a constant background. Three Gaussian lines represent the molecular orbital-related peaks, while the constant and the two remaining Gaussians were used to match the background of the spectra (tails at the negative and positive boundaries of the voltage interval). The dashed lines in Fig. 2 show the results of these fits. The positions of the HOMO, LUMO, and LUMO+1 maxima, that were extracted from the fit, are summarized in Table I. Comparison of fits to the experimental data with manually modified maxima positions leads to the error bars for the energies.

We must note that the dI/dV spectra do not necessarily coincide with the local density of states of the sample. For tunneling voltages which are of comparable magnitude to the tip and the sample work functions the voltage-dependent transmission coefficient has to be taken into account.^{25,26} This is the case in our measurements, where the voltage interval comprises values between -3 and $+3$ V. In order to recover a more accurate local density of states of the sample, it has been suggested to normalize the experimentally acquired dI/dV spectra to the tunneling transmission probability.²⁷ In our data analysis we approximated the actual transmission probability by fitting an exponential to the 1 ML spectrum background, i.e., to data points at 0.1 , 1.4 , and 2.5 eV, and analogously to the 0.5 ML spectrum background. Such normalization of the spectrum varies the position of the molecular orbital-related peaks by less than the error bars given in Table I.

From the values in Table I we can calculate the HOMO-LUMO gap as $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} = 2.68 \pm 0.03$ eV for 0.5 ML and $\Delta E = 2.71 \pm 0.03$ eV for 1.0 ML. Within the error bars we obtain the same gap width for the two different coverages, which in turn is also consistent with the value $\Delta E = 2.7 \pm 0.2$ eV found for individual molecules on Au(111).¹⁶ However, the energy positions of the molecular orbital-associated peaks at the higher coverage are shifted uniformly toward negative energies. For the HOMO we obtain $E_{\text{HOMO}}(0.5 \text{ ML}) - E_{\text{HOMO}}(1.0 \text{ ML}) = 0.12 \pm 0.04$ eV, for the LUMO $E_{\text{LUMO}}(0.5 \text{ ML}) - E_{\text{LUMO}}(1.0 \text{ ML}) = 0.09 \pm 0.02$ eV, and for the LUMO+1 $E_{\text{LUMO+1}}(0.5 \text{ ML}) - E_{\text{LUMO+1}}(1.0 \text{ ML}) = 0.13 \pm 0.02$ eV.²⁸ Such homogeneous downward shift is again consistent with the single molecule STS peaks located at $E_{\text{HOMO}}(\text{molecule}) = -1.7 \pm 0.2$ eV and $E_{\text{LUMO}}(\text{molecule}) = 1.0 \pm 0.2$ eV (Ref. 16) (see Table I).

FIG. 3. Photoemission spectra of the C 1s core level as a function of C₆₀ coverage. As discussed in the text, the large core-level shifts for 3 ML might be explained by photohole screening effects. The inset shows the high resolution spectra of the C 1s satellite structure in 3 ML C₆₀/Au(887) taken at $h\nu=300$ eV.

The value of the HOMO-LUMO gap in Fig. 2 is significantly reduced from the one determined for thick layers of C₆₀ on Au(111) in photoemission experiments,¹⁴ and thus much closer to the ≈ 2 eV value found for exciton energies and density functional theory (DFT) calculations of the ground state (N electron systems).^{16,29} This indicates a better screening of the $N\pm 1$ quasiparticle state in STS and photoemission for the C₆₀ monolayer compared to the thick film, probably due to the proximity of the metal surface in the former. The rigid shift of the STS spectrum from 0.5 to 1 ML (Fig. 2) cannot be explained by changes in screening, since these lead to LUMO and HOMO shifts in the opposite directions.³⁰ The homogeneous shift in the whole band structure is characteristic of metal/insulator or metal/semiconductor interfaces,³¹ where the relative position of the Fermi energy varies within the gap, depending on the density and distribution of gap states and the amount of charge being transferred inside them.³² Such gap states, which are detected in the absorption experiments presented below, are not observed in tunneling spectra. A possible explanation is given in Sec. III C.

B. Photoemission: Core levels and valence band

Figures 3 and 4, respectively, show the C 1s core-level and the valence band spectra for the C₆₀/Au(887) system. The data are generally consistent with previous photoemission work of C₆₀ on flat Au(111),²⁰ except the LUMO peak at the Fermi level, which is absent in our spectra. The solid C₆₀ features are already observed in the 2–3 ML range. In the valence band, the 2 ML spectrum is identical to the thick C₆₀ layer spectrum taken at the same photon energy.^{20,33} In the C 1s core level, the 3 ML peak is analogous to that of the thick film, as judged from the multiple satellite structure observed in the high resolution spectrum shown in the inset of Fig. 3. The interest is focused on the coverage-dependent shift of the C 1s and HOMO peaks. The C 1s peak at 284.6 eV for 0.5 ML shifts by 50 meV to higher binding energies for 1 ML and by 500 meV for 3 ML. Similarly, in the valence band in Fig. 4(a) the HOMO peak at -1.7 eV for 0.5 ML smoothly evolves into a stronger peak at -2.0 eV beyond 1 ML. Noting the uncertainty (0.1 eV) in the spectra of Fig. 3, the C 1s shift from 0.5 to 1 ML is comparable to the

FIG. 4. (Color) Valence band photoemission spectra for C₆₀/Au(887) layers of different thicknesses. As a function of coverage, the C₆₀ HOMO peak grows whereas the two Au(887) surface states S1 and S2 are quenched.

≈ 100 meV charge transfer shift observed in the STS spectra. However, the large (0.3–0.5 eV) negative shift in the HOMO and the C 1s peaks which characterizes thicker films, together with the 0.5 eV positive shift observed in inverse photoemission,¹⁵ supports the hypothesis that strong final state effects build up in photoemission beyond 1 ML, making it difficult to determine actual HOMO-LUMO gap changes.

The two strongest features in the clean Au(887) valence band spectrum belong to the Au Shockley surface state and to a surface-potential derived emission,³⁴ at -0.45 eV (S1) and -2.45 eV (S2), respectively. Both decrease with increasing coverage and disappear with the full monolayer. At this coverage, the valence band spectrum close to E_F is flat, and hence there is no evidence for a LUMO-related peak at the Fermi edge. That is consistent with the LUMO position in the STS data of Fig. 2, but disagrees with the feature observed in 1 ML C₆₀ on Au(111).²⁰

C. NEXAFS: Gap states

NEXAFS and photoemission spectra were taken together in order to check for possible C₆₀ fragmentation due to the x-ray beam. The last PE spectra in the series were taken at the very surface sensitive photon energies of 50 eV. They

FIG. 5. Near-edge x-ray absorption spectra at the carbon 1s edge of C₆₀ on Au(887). The filled Gaussian denotes the transition into the HOMO-LUMO gap states of 0.5 ML C₆₀/Au(887).

FIG. 6. Band diagrams for C_{60} coverages of 0.5 ML (left panel) and 1 ML (right panel) on Au(887). For the latter we assume the absence of charge transfer and interfacial dipoles, and hence vacuum level (VL) alignment. For clusters, the presence of gap states allows the electron transfer from the substrate, which in turn leads to an interface dipole.

did not indicate changes from the usual valence band spectra. Therefore we can exclude the possibility of photolysis in NEXAFS and core-level photoemission. Figure 5 shows the C 1s NEXAFS spectra for the C_{60} /Au(887) system. As found in photoemission spectra, the NEXAFS peaks for 1 and 3 ML are analogous to those for C_{60} /Au(111).^{18,20,35} They are also consistent with the STS spectra in Fig. 2, allowing a straightforward peak assignment. The influence of the noble metal surface on the energy position and intensity of the π^* -derived exciton peaks is negligible, as deduced by the direct comparison of the spectra at different coverages. However, by fitting Gaussian lines to the spectra, we find that the full width at half maximum (FWHM) of the LUMO-related peak decreases from 0.33 eV at 0.5 ML to 0.18 eV at 3 ML. We only observe a slight attenuation of the LUMO+1 peak for a coverage up to 1 ML, as observed in Au(111),²⁰ but no change in the peak position. This further proves that the core-level and HOMO/LUMO shifts in photoemission and inverse photoemission are not due to changes in the structure of molecular levels,¹⁵ but rather to screening and charge transfer effects.

The 0.5 ML ordered cluster spectrum in Fig. 5 reveals a new feature on the low energy side of the LUMO exciton, i.e., inside the HOMO-LUMO gap, which is not detected in STS (Fig. 2). Such gap state, also observed at submonolayer C_{60} coverages on Au(111) (not shown), is strongly quenched in thicker films, and hence it cannot be explained as due to molecule fragmentation effects. Furthermore, the gap state feature makes the 0.5 ML spectrum similar to the NEXAFS spectra of thin LiCl and KCl insulating layers grown on Cu(111).^{36,37} In the latter, the gap feature was attributed to absorption into metal induced gap states (MIGSs), i.e., electronic states induced by the Cu substrate inside the insulator band gap, with an extremely local (atomic) character, as proven by the separate analysis of K and Cl absorption edges in KCl/Cu(111).³⁷ However, in contrast to the MIGS intensity which saturates beyond 1 ML in the KCl/Cu(111) interface, the intensity of the gap state in Fig. 5 is attenuated by a factor of 20 at monolayer coverage and completely quenched in thicker films. Since the gap state is also observed in C_{60} /Au(111) at fractional coverages, it cannot be related to a particular interfacial electronic property of the highly periodic C_{60} superstructure, but rather to C_{60} clusters with a reduced number of molecules. In this context, the gap states in Fig. 5 could be associated with C_{60} molecules with different

lateral coordinations, such as isolated molecules or those defining the edges of fullerene islands in the regular superstructure. Such molecules may play the same role as defects in metal/insulator interfaces, which are known to induce a continuum of states inside the gap.³¹

We address now the absence of spectroscopic signatures of the interfacial states in the tunneling spectra (Fig. 2). The strict interfacial character of the gap states may be responsible for this observation. Since the dI/dV signal is proportional to the sample density of states at the tip position,³⁸ which is ≈ 1 nm above the interface, and since the interfacial states are spatially decaying into vacuum, it may occur that their contribution to the tunneling spectra falls below the detection limit of the instrument. Tunneling spectra of 0.5 ML C_{60} on Au(887) acquired on molecules either located at the boundary or embedded in the rectangular islands revealed the same shape, and hence no signature of interfacial states. Another surface-localized state is the Au(887) surface state (S1, see Fig. 4) which in dI/dV spectra is clearly visible for the clean surface. For C_{60} -covered surfaces, however, the spectroscopic signature of the surface state is no longer detectable, further supporting the argument that the spectroscopic signature of surface-localized and interface-localized states is difficult to be accessed if the tip position is located far from the interface.

The band diagram shown in Fig. 6 describes the C_{60} /Au(887) system, in agreement with our STS and absorption experiments. The model assumes the absence of charge transfer and interfacial dipoles for 1 ML, such that metal and molecule vacuum levels are aligned.^{31,39} The key feature is the presence of interfacial gap states that fill up the HOMO-LUMO gap for 0.5 ML and are detected in NEXAFS. A density of states inside the gap allows the transfer of charge from the Au substrate, and hence the formation of an interfacial dipole. For 1 ML, gap states disappear and the charge is transferred back to the Au substrate. The negative (electron) charge transfer back to the substrate explains the rigid downward shift of the HOMO- and LUMO-related peaks as observed in STS (and eventually, in photoemission), since these are always referred to the metal Fermi level.

IV. CONCLUSIONS

A combination of techniques as diverse as PES, NEXAFS, and STS was used to study the electronic structure of

C₆₀ on Au(887). Core-level and valence band PES results are generally consistent with previous work on the C₆₀/Au(111) system, although we were unable to detect LUMO-related Fermi level features. The interesting results concern STS and NEXAFS. Upon increasing the C₆₀ coverage, the STS data show a uniform shift of molecular orbital-related peaks toward negative binding energies, such that the width of the HOMO-LUMO gap remains constant. We have also identified a characteristic gap state peak inside the HOMO-LUMO gap in the 0.5 ML NEXAFS spectrum, which is appreciably quenched for 1 ML coverage. This suggests that gap states which characterize the highly ordered C₆₀ clusters on Au(887) are associated with isolated molecules or cluster edges that allow a local surface-molecule charge transfer. Further absorption experiments varying the light polarization should be carried out to confirm the dipole nature of such gap state.

ACKNOWLEDGMENTS

We want to thank A. Rubio (University of the Basque Country San Sebastián), F. Himpsel (University of Madison, WI), and I. Jiménez (Instituto de Ciencia y Tecnología de Polímeros Madrid) for useful discussions, and Cinzia Cepek (TASC, INFN-CNR Trieste, Italy) for providing clean C₆₀. This work was financed as part of the European Science Foundation EUROCORES Programme SONS (MAT2002-12241-E and MAT2002-11975-E) and a Marie Curie Intra-European fellowship within the sixth European Community framework programme. Further support was obtained from the Comunidad Autónoma de Madrid (Grant No. GR-MAT/0022/2004). This work was performed at the Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland and at synchrotron Elettra, Trieste, Italy. The synchrotron access was supported by the European Community-Research Infrastructure Action under the FP6 "Structuring the European Research Area" Programme [through the key actions (i) Integrated Infrastructure Initiative "Integrating Activity on Synchrotron and Free Electron Laser Science" and (ii) Strengthening the European Research Area, Research Infrastructures Contract No. (RII3-CT-2004-506008)].

¹G. P. Lopinski, D. D. M. Wayner, and R. A. Wolkow, *Nature* (London) **406**, 48 (2000).

²J. I. Pascual, J. V. Barth, G. Ceballos, G. Trimarchi, A. De Vita, K. Kern, and H.-P. Rust, *J. Chem. Phys.* **120**, 11367 (2004).

³R. Otero, Y. Naitoh, F. Rosei, P. Jiang, P. Thstrup, A. Gourdon, E. Lægsgaard, I. Stensgaard, C. Joachim, and F. Besenbacher, *Angew. Chem., Int. Ed.* **43**, 2092 (2004).

⁴J.-L. Lin, D. Y. Petrovykh, A. Kirakosian, H. Rauscher, F. J. Himpsel, and P. A. Dowben, *Appl. Phys. Lett.* **78**, 829 (2001).

⁵C. Preinesberger, G. Pruskil, S. K. Becker, M. Dähne, D. V. Vyalikh, S. L. Molodtsov, C. Laubschat, and F. Schiller, *Appl. Phys. Lett.* **87**, 083107 (2005).

⁶V. Repain, G. Baudot, H. Ellmer, and S. Rousset, *Europhys. Lett.* **58**, 730 (2002).

⁷N. Néel, J. Kröger, and R. Berndt, *Adv. Mater.* (Weinheim, Ger.) **18**, 174 (2006).

⁸*The Fullerenes*, edited by H. W. Kroto, J. E. Fischer, and D. E. Cox (Pergamon, Oxford, 1993).

⁹A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, *Nature* (London) **350**, 600 (1991).

¹⁰K. Holczer, O. Klein, G. Grüner, S.-M. Huang, R. B. Kaner, K.-J. Fu, R. L. Whetten, and F. Diederich, *Science* **252**, 1154 (1991).

¹¹B. W. Hoogenboom, R. Hesper, L. H. Tjeng, and G. A. Sawatzky, *Phys. Rev. B* **57**, 11939 (1998).

¹²A. J. Maxwell, P. A. Brühwiler, D. Arvanitis, J. Hasselström, M. K.-J. Johansson, and N. Mårtensson, *Phys. Rev. B* **57**, 7312 (1998).

¹³R. Hesper, L. H. Tjeng, and G. A. Sawatzky, *Europhys. Lett.* **40**, 177 (1997).

¹⁴R. Schwedhelm, L. Kipp, A. Dallmeyer, and M. Skibowski, *Phys. Rev. B* **58**, 13176 (1998).

¹⁵T. R. Ohno, Y. Chen, S. E. Harvey, G. H. Kroll, J. H. Weaver, R. E. Haufler, and R. E. Smalley, *Phys. Rev. B* **44**, 13747 (1991).

¹⁶X. Lu, M. Grobis, K. H. Khoo, S. G. Louie, and M. F. Crommie, *Phys. Rev. B* **70**, 115418 (2004).

¹⁷C. Cepek, A. Goldoni, and S. Modesti, *Phys. Rev. B* **53**, 7466 (1996).

¹⁸K.-D. Tsuei, J.-Y. Yuh, C.-T. Tzeng, R.-Y. Chu, S.-C. Chung, and K.-L. Tsang, *Phys. Rev. B* **56**, 15412 (1997).

¹⁹G. K. Wertheim and D. N. E. Buchanan, *Phys. Rev. B* **50**, 11070 (1994).

²⁰C.-T. Tzeng, W.-S. Lo, J.-Y. Yuh, R.-Y. Chu, and K.-D. Tsuei, *Phys. Rev. B* **71**, 2263 (2000).

²¹E. I. Altman and R. J. Colton, *Phys. Rev. B* **48**, 18244 (1993).

²²C. Rogero, J. I. Pascual, J. Gómez-Herrero, and A. M. Baró, *J. Chem. Phys.* **116**, 832 (2002).

²³V. Repain, J. M. Berroir, S. Rousset, and J. Lecoeur, *Europhys. Lett.* **47**, 435 (1999).

²⁴M. Grobis, X. Lu, and M. F. Crommie, *Phys. Rev. B* **78**, 161408(R) (2002).

²⁵A. Selloni, P. Carnevali, E. Tosatti, and C. D. Chen, *Phys. Rev. B* **31**, 002602 (1985).

²⁶N. D. Lang, *Phys. Rev. B* **34**, 5947 (1986).

²⁷V. A. Ukraintsev, *Phys. Rev. B* **53**, 11176 (1996).

²⁸Since the binding energies of spectroscopic features can depend on the electric field between the tip and the sample, as was shown for the Shockley surface states of the (111) surfaces of Ag, Au, and Cu [L. Limot, T. Maroutian, P. Johansson, and R. Berndt, *Phys. Rev. Lett.* **91**, 196801 (2003); J. Kröger, L. Limot, H. Jensen, R. Berndt, and P. Johansson, *Phys. Rev. B* **70**, 033401 (2004)], we acquired analogous spectra for decreasing tip-sample distances (up to tunneling currents of 100 nA). A shift of the molecular orbital-related peaks, however, stayed below the detection limit. As a consequence we rule out any electric-field-related effects in the tunneling junction to drive the observed orbital energy shift.

²⁹C. Hartmann, M. Zigone, G. Martinez, E. L. Shirley, L. X. Benedict, S. G. Louie, M. S. Fuhrer, and A. Zettl, *Phys. Rev. B* **52**, R5550 (1995).

³⁰J. E. Ortega, F. J. Himpsel, D. Li, and P. A. Dowben, *Solid State Commun.* **91**, 807 (1994).

³¹W. Mönch, *Semiconductor Surfaces and Interfaces*, Springer Series in Surface Science Vol. 26, 2nd eds. (Springer-Verlag, 1995).

³²C. Laubschat, M. Prietsch, M. Domke, E. Weschke, G. Remmers, T. Mandel, J. E. Ortega, and G. Kaindl, *Phys. Rev. Lett.* **62**, 1306 (1989).

³³C. Ton-That, A. G. Shard, S. Egger, V. R. Dhanak, and M. E. Welland, *Phys. Rev. B* **67**, 155415 (2003).

³⁴H.-G. Zimmer, A. Goldmann, and R. Courths, *Surf. Sci.* **176**, 115 (1986).

³⁵P. A. Brühwiler, A. J. Maxwell, P. Rudolf, C. D. Gutleben, B. Wästberg, and N. Mårtensson, *Phys. Rev. Lett.* **71**, 3721 (1993).

³⁶M. Kiguchi, R. Arita, G. Yoshikawa, Y. Tanida, M. Katayama, K. Saiki, A. Koma, and H. Aoki, *Phys. Rev. Lett.* **90**, 196803 (2003).

³⁷M. Kiguchi, G. Yoshikawa, S. Ikeda, and K. Saiki, *Phys. Rev. B* **71**, 153401 (2005).

³⁸J. Tersoff and D. R. Hamann, *Phys. Rev. Lett.* **50**, 1998 (1983).

³⁹H. Ishii, K. Sugiyama, E. Ito, and K. Seki, *Adv. Mater.* (Weinheim, Ger.) **11**, 605 (1999).