ELSEVIER

Electronic structure of K doped C_{60} monolayers on Ag(001)

C. Cepek [a,b,*], M. Sancrotti [a], T. Greber [b], J. Osterwalder [b]

[a] *Laboratorio Nazionale TASC–INFM, Padriciano 99, 34012 Trieste, Italy*
[b] *Physik-Institut, Universität Zürich, 8057 Zürich, Switzerland*

Abstract

The doping of a C_{60}/Ag(100) interface with K is studied by high resolution valence band photoemission spectroscopy. With increasing potassium exposure the progressive filling of the C_{60} lowest unoccupied molecular orbital (LUMO) derived band is observed. The charge transfer onto the C_{60} molecules is quantified from the observed binding energies of the LUMO derived band. Up to a half filled LUMO no rigid band shift is found. Furthermore the intensity of the highest occupied molecular orbital is not constant but shows in normal emission a pronounced dip between half and complete LUMO filling. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Alkali metals; Fullerenes; Photoelectron spectroscopy

1. Introduction

Close cage C_{2n} ($n > 9$) molecules (fullerenes) constitute the building blocks for a new class of materials that have attracted much interest over the past 10 years [1]. In alloys they do, however, not only act like giant noble gas atoms but their internal vibration modes and the high electron affinities give rise to negative ion formation with strong electron–phonon interactions [2]. The superconducting K_3C_{60} fulleride is a good example of this interplay and its consequences. The electronic structure of such fullerite compounds can be described in a charge transfer picture where the lowest unoccupied molecular orbital (LUMO) of C_{60} is filled in doping it, for example, with alkali metals. It has a degeneracy of six and depending on the charge transfer (e.g. three for

K_3C_{60}) metals or ionic insulators (K_6C_{60} and K_4C_{60}) may be formed.

At noble metal surfaces the strong polarizability and the large electron affinity (-2.65 eV) yield to electron transfer on C_{60} upon adsorption where a low work function surface favors the charge transfer [3]. For the electronic structure it is important to know how many electrons are transferred on the C_{60} molecules. Furthermore the extent to which the molecular orbitals shift with respect to the Fermi level is essential in order to understand the response of the C_{60} molecules upon doping. A rigid shift of all molecular derived bands indicates, for instance, that Coulomb interaction dominates the doping and that the internal symmetry of the molecule persists. A deviation from a rigid band shift on the other hand implies orbital dependent bonding to the substrate.

Here an experiment is reported where one monolayer (ML) of C_{60} on Ag(001) is exposed to a constant flux of potassium atoms during a high resolution photoemission experiment. With

---

* Corresponding author. Fax: +39-040-226767.
E-mail address: cepek@sci.area.trieste.it (C. Cepek)

increasing potassium coverage the photoemission indicates a continuous increase of the LUMO binding energy up to complete filling. In this respect the findings are consistent with the literature [4]. We do, however, find a significant deviation from the rigid band shift model and a pronounced dip in the photoelectron yield in the highest occupied molecular orbital (HOMO).

2. Experimental

Measurements were performed in VG ESCALAB 220 spectrometer [5]. The valence band photoemission spectra were recorded with an overall energy resolution of 100 meV and an angular resolution of $\sim 5°$. The photon source was a monochromatized microwave-driven high flux He discharge lamp (Gammadata Burklint AB, Sweden), which recovers spectral features in the wing of the thermally excited electrons above the Fermi level up to 5 kT. The photon flux was reduced by a factor of 10, to ca. 5×10^{12} photons cm^{-2} s^{-1}, in order to avoid light damage of the sample [6].

C_{60} powder (99.9%) was sublimated from a titanium crucible using an evaporation rate of ~ 0.2 ML min^{-1}. The ordered monolayer was obtained by evaporating C_{60} on the Ag(100) surface at 600 K. In this case the C_{60} molecules form on the surface a close packed compact layer, presenting a $c(6 \times 4)$ low energy electron diffraction (LEED) pattern, in which the C_{60}–C_{60} distance is ~ 10.4 Å [7,8].

Potassium was evaporated during the photoemission experiments from a well out-gassed SAES getter source housed in a water-cooled cage, whose aperture can be opened with a movable shutter. In order to minimize the magnetic fields induced by the current across the getter source, the current was guided close behind the getter source back to the electrical feedthrough. The K flux adsorbed on the sample was 1×10^{11} K atoms cm^{-2} s^{-1} if the complete LUMO filling requires 4.3 K atoms/C_{60}. From the linear decrease of the work function up to complete LUMO filling at fixed K flux and the constant potassium uptake as measured by X-ray photon spectroscopy we presume a constant sticking coefficient of K on C_{60}/Ag(100). The valence band photoemission spectra were collected while evaporating K on the C_{60} ML at room temperature. The acquisition time for every spectrum is 2 min and the corresponding K coverage varies by ca. 0.01 ML of K within one spectrum. The measurements shown have been reproduced several times.

3. Result and discussion

Fig. 1 shows the evolution of the valence band spectra of 1 C_{60}ML on the Ag(100) as a function of K exposure. At the bottom the clean Ag(100) surface and a thick C_{60} multilayer film (>5 ML) spectra are shown for comparison. The spectrum of Ag(001) is shown in order to demonstrate that down to the onset of the 4d bands the spectrum is flat and negligible if the strong attenuation by the C_{60} layer is considered. All binding energies are referred to the Fermi level of polycrystalline silver. While in solid C_{60} the LUMO is unoccupied, it gets more and more occupied after adsorption on

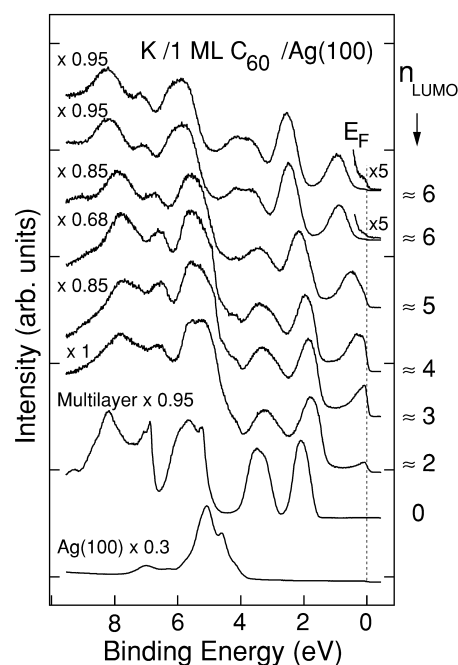

Fig. 1. Valence band photoemission spectra of 1 C_{60} ML on Ag(100) surface as a function of K doping. Also shown are the spectra of the clean Ag(100) surface and a C_{60} multilayer.

Ag(001) and upon further doping with potassium. In going from the bottom to the top of Fig. 1 the gradual filling of the LUMO band can be followed. Here n_{LUMO} indicates the number of electrons in the C_{60} LUMO derived band (see below). The doping level where the C_{60} LUMO is half filled ($n_{LUMO} = 3$) has been determined from the crossing of the LUMO peak with the Fermi level. This assignment of maximum intensity at half filling presumes for $n_{LUMO} = 3$ an unsplit LUMO band with maximum density at its center of gravity. This assumption is supported by the present findings (see Fig. 1) and those from bulk K_xC_{60} phases at room temperature [9,10]. The crossing point has been found by interpolation of the LUMO maxima above and below the Fermi level as shown in Fig. 2. These maxima were found after division of the data by an experimentally determined Fermi edge from polycrystalline silver. The LUMO is fully occupied ($n_{LUMO} = 6$) at the point where the photoemission spectrum does not show further significant emission from the Fermi level and where the LUMO peak has a binding energy of ~ 0.9 eV, as in K_6C_{60} [9,10]. For higher K exposures the intensity at the Fermi level recovers, probably due to metallic K. After annealing of such an 'over-doped' sample (see top spectrum in Fig. 1) for 5 min to $\sim 100°C$ the spectra become indistinguishable from the $n_{LUMO} = 6$ spectrum without intensity at the Fermi level. Such an annealing for $n_{LUMO} < 6$ sample does not produce significant changes in the spectra. Supposing a linear relationship between the K adsorption rate and n_{LUMO}, and with the two fixpoints for $n_{LUMO} = 3$ and $n_{LUMO} = 6$, we find that in the undoped monolayer C_{60} on Ag(001) 1.7 ± 0.08 electrons are transferred from the Ag(100) substrate onto the C_{60} molecules. This value is lower than that of 2.7 ± 0.5 as evaluated from the energy shift of the C_{60} vibrational modes [5]. However, the high resolution electron energy loss spectroscopy (HREELS) method may overestimate the C_{60} charge state, because energy shifts of the vibrational modes can also be induced by breaking of the molecular symmetry after adsorption — as a deviation from the rigid band shift indicates (see below) [3,12,13]. The value of 1.7 transferred electrons found in this work coincides, however, with that observed in
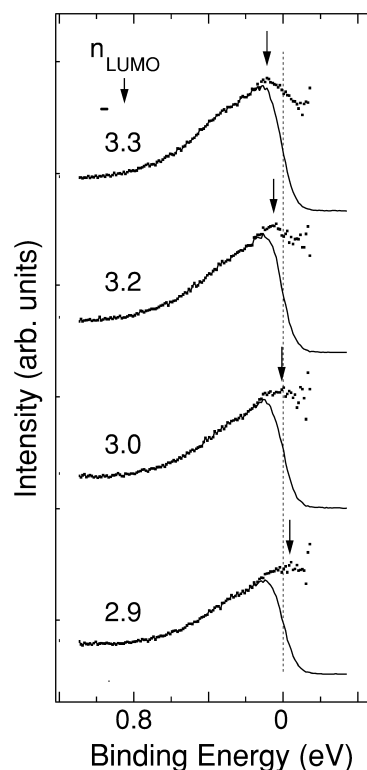

Fig. 2. Valence band photoemission spectra around the Fermi level for different K exposures before (—) and after normalization with the Fermi function (···). Half filling of the LUMO ($n_{LUMO} = 3$) is allocated to the crossing of the LUMO maximum with the Fermi level. For details see text.

1 ML C_{60} on polycrystalline Ag [4]. It has, however, to be noted that if we apply the same procedure as Ref. [4], that is, one fix point ($n_{LUMO} = 6$) and the integrated LUMO intensity, we would get a number of 0.9 electrons transferred onto the C_{60} molecules(see Figs. 2 and 3b). This value is close to 0.75 as found with the integration method for C_{60} on Ag(111) [11]. Below it will be shown that the integration method may be hampered by the variation of the partial photoemission cross-section.

In order to better understand the electronic properties of the K doped monolayer, we determined the LUMO and HOMO binding energies and normal emission intensities as a function of K doping. The peak integrals were evaluated after the subtraction of a Shirley background and the
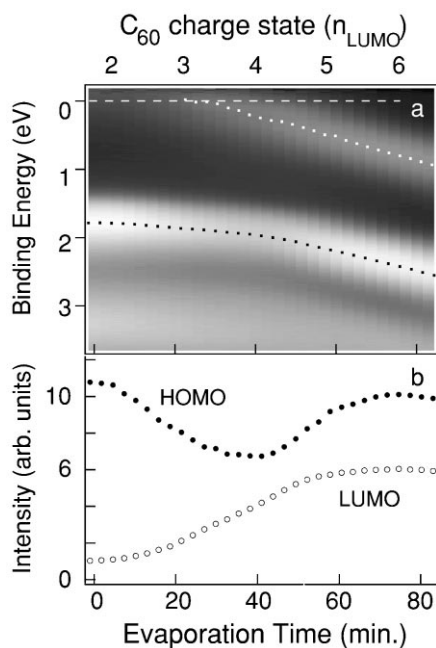
Fig. 3. (a) Gray scale two-dimensional plot of valence band spectra given as a function of the binding energy and the C_{60} charge state. White and black dots refer to the C_{60} LUMO and HOMO peaks. (b) Integrated intensity of the LUMO (○) and HOMO (●) emissions as a function of the K evaporation time.

peak binding energy from the position of the peak maxima after normalizing the spectra with the experimental Fermi function. The results are shown in Fig. 3a and b, where the photoemission intensity is displayed on a linear gray scale as a function of binding energy and evaporation time (bottom scale) and the LUMO filling (top scale). The open dots refer to the LUMO, while the filled dots to C_{60} HOMO related properties.

In Fig. 3a it can be clearly seen that a rigid band shift is not followed for $n_{LUMO} < 3$. In fact, for $n_{LUMO} < 3$ the C_{60} LUMO binding energy increases stronger with K coverage than the C_{60} HOMO binding energy (0.3 and 0.1 eV/e$^-$ doping, respectively). Only for $n_{LUMO} > 4$ a rigid shift of HOMO and LUMO (0.3 eV/e$-$) is observed. At the same coverage of $n_{LUMO} = 4$, the C_{60} HOMO yield passes a minimum, not found in the yield from the LUMO method. We are tempted to assign this to a distinct two-dimensional 'K_4C_{60}' like (tetravalent) phase. Since the HOMO yield

increases for $n_{LUMO} > 4$ again, this 30% effect can not be attributed to inelastic scattering. The occupancy of the HOMO is constant (10 electrons) and therefore the photoemission matrix element for normal emission has to vary as a function of doping. The extent to which this is an initial or a final state effect cannot be decided at the present stage of analysis. It is, nevertheless, a clear indication that the integral method for the determination of the C_{60} charge state may be hampered since such intensity variations may affect the LUMO photoemission matrix element as well. If we speculate that diffraction influences the final state wave function it may cause partial loss/or gain in a certain direction. Experiments on single crystal samples should therefore be particularly affected [11]. On polycrystalline samples, on the other hand the work function induced differences will allow only an average n_{LUMO} determination [4].

4. Conclusions

In conclusion a new method for the quantitative determination of the charge transfer on C_{60} upon adsorption is proposed. For Ag(001) the method indicates 1.7 electrons are transferred from the substrate onto C_{60}. In the doping regime below $n_{LUMO} = 3$ the LUMO shifts stronger in energy than the HOMO. This non-rigid band shift indicates the C_{60} molecules become distorted in this doping regime.

References

[1] H. Enrenreich, F. Spaepen (Eds.), Solid State Physics vol. 48, Academic Press, New York, 1994.
[2] O. Gunnarsson, Rev. Modern Phys. 69 (1997) 575.

[3] P. Rudolf, in: H. Kuzmany, J. Fink, H. Hehring, S. Roth
    (Eds.), Proceeding of the Xth International Winterschool
    on Electronic Properties of Novel Materials, World Scien-
    tific, Singapore, 1996.

[4] B.W. Hoogenboom, R. Hesper, L.H. Tjieng, G.A.
    Sawatzky, Phys. Rev. B 57 (1998) 11939.

[5] T. Greber, O. Raetzo, T.J. Kreutz, P. Schwaller, W. Deich-
    mann, E. Wetli, J. Osterwalder, Rev. Sci. Instrum. 68
    (1997) 4549.

[6] C. Cepek, T. Greber, M. Sancrotti, J. Osterwalder, unpub-
    lished data.

[7] A. Goldoni, C. Cepek, E. Magnano, A.D. Laine, S.
    Vandré, M. Sancrotti, Phys. Rev. B 58 (1998) 2228.

[8] E. Giudice, E. Magnano, S. Rusponi, C. Boragno, U. Val-
    busa, Surf. Sci. 405 (1998) L561–L565.

[9] M. Merkel, M. Knufer, M.S. Golden, J. Fink, R. Seemann,
    R.L. Johnson, Phys. Rev. B 47 (1993) 11470.

[10] P.J. Benning, P. Stepniak, J.H. Weaver, Phys. Rev. B 48
    (1993) 9086.

[11] L.H. Tjieng, R. Hesper, A.C.L. Heessels, A. Heeres, H.T.
    Jonkman, G.A. Sawatzky, Solid State Commun. 103
    (1997) 31.

[12] B.P. Feuston, W. Andreoni, M. Parinello, E. Clementi,
    Phys. Rev. B 44 (1991) 4056.

[13] C. Cepek, P. Schiavuta, M. Sancrotti, H. Pedio, Phys. Rev.
    B 60 (2068) 1999.