Charge-transfer dynamics in one-dimensional C$_{60}$ chains

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1. Introduction

Self-assembly is a promising method for the integration and patterning of molecular electronic devices with complex circuits at the nanoscale [1,2]. Vicinal surfaces, which exhibit a regular distribution of steps and terraces, are natural templates to guide the assembly of molecules into specific arrangements [3–7]. The convenient orientation of steps and terraces, are natural templates to guide the assembly of molecules into specific arrangements [3–7]. The convenient orientation of steps and terraces, are natural templates to guide the assembly of molecules into specific arrangements [3–7].

C$_{60}$ molecules attract a lot of interest because of their prospective role in nanoelectronics [11] and because of the rich transport properties in the solid phase, ranging from metallic to Mott–Hubbard insulating and superconducting behavior, when doped with alkaline metals [12]. Due to the high electron affinity of the molecule, adsorption on metal surfaces may also produce a partial filling of the C$_{60}$ LUMO (lowest unoccupied molecular orbital) through charge transfer from the substrate [13–15]. Very promising was the observation of an excitation gap persisting up to 260 K for C$_{60}$/Ag(100), although its superconductor origin is not demonstrated [16–18]. The interaction of the C$_{60}$ molecule with the substrate is also decisive in determining its orientation and intermolecular distance. Orientational order was a necessary condition to determine the LUMO band structure in a K$_3$C$_{60}$ layer on Ag(1 1 1) [19]. The dispersion of the C$_{60}$-derived states close to the Fermi level was found to be consistent with band structure calculations renormalized due to the coupling with high-energy phonons.

C$_{60}$ on Cu(553) is possibly a good system to study correlation effects and electron-lattice interactions in a one-dimensional molecular system. Tamai et al. have shown that on this vicinal surface, the molecules self-assemble into long-ordered single chains [8,10]. Scanning tunneling microscopy (STM) images display alternating bright and dim rows of molecules. Adjoining chains have a different bonding to the ascending step and molecules are adsorbed either with the hexagon or the pentagon ring facing the substrate terraces (Fig. 1). The presence of a regular array of atomic steps in the surface induces a 4% expansion of the molecular layer in the direction perpendicular to the chains, compared to the solid phase. Angle-resolved photoemission (ARPES) data show that this small increase of the C$_{60}$–C$_{60}$ distance is sufficient to produce a very anisotropic band structure, indicative of significantly decoupling of the molecular chains. Along the chains, the HOMO (highest occupied molecular orbital) exhibits up to 400 meV electronic dispersion, whereas in the perpendicular direction the bandwidth is lower than 30 meV [10]. Because of charge transfer from the metal substrate, the LUMO is partially occupied and contributes to the density of states near the Fermi level. Its photoemission lineshape...
is very different from the typical LUMO spectra for two-dimen-
sional C60 layers: there is a gradual loss of intensity towards the
Fermi level and no sharp quasi-particle peak appears. Systematic
ARPES measurements display no periodic dispersion near the
Fermi level [20].

In order to better understand the molecule–molecule and mol-
ecule–substrate electron hopping mechanism, we investigated the
C60 chains by resonant photoemission, also referred to as autoion-
ization [21–23]. From the decay process of an electron excited from
a core level to the LUMO it is possible to deduce the electron hop-
ping time-scale for that electron by comparison with the core level
lifetime. If the electron is transferred to a neighboring molecule or
to the substrate faster than the core level lifetime, the HOMO par-
ticipant channel is quenched. With this technique, Maxwell et al.
proved the hybridization of the core-hole perturbed C60 orbitals
and the sp band of the metal substrate in C60/Cu(110) [24]. The
directional character of the π* orbitals that form the LUMO in C60
allows tuning the excitation to different parts of the C60 molecule
by selecting the direction of the light polarization vector, as dem-
onstrated by Maxwell et al. for C60/Al(110) [25]. We take advan-
tage of this fact as a complementary method to investigate possi-
ble anisotropy in the LUMO derived intermolecular interac-
tions in the directions parallel and perpendicular to the C60 chains.
Our results show that in the case of 0.9 ML C60/Cu(553) the aniso-
tropic intermolecular interaction can not be disentangled from the
interaction of the molecules with the substrate. No dependence of
the substrate–molecule interaction on the light polarization vector
is observed.

2. Experimental details

The photoemission and absorption measurements were per-
formed at the surface and interface spectroscopy (SIS) beamline
at the Swiss Light Source, Paul Scherrer Institut (Villigen, Switzer-
land). Linear vertical and horizontally polarized light was used. The
photoemission spectra were recorded with a Gammadata Scienta
2002 analyzer in angle integration mode. The electron energy res-
olution in the photoemission data was 140 meV and the photon
energy resolution in the absorption data was 100 meV. The photon
energy was calibrated using the 3p3/2 core level measured in the
clean Cu substrate and the Cu Fermi level measured at the same
photon energy, hν = 275 eV. All the data were acquired at room
temperature (RT) and the pressure during the measurements re-
mained below 2 × 10−10 mbar.

Cu(553), the stepped surface used in this work, is a B-type vic-
nial of Cu(111) with a miscut angle of 12.3°. It is composed of
(111) terraces separated by monoatomic steps with (111) step
facets. The nominal terrace width is 9.8 Å, which is close to the
van der Waals diameter of the C60 molecule. The Cu(553) single
crystal was cleaned by several cycles of argon ion sputtering at
1000 V and 700 V and annealing at 700 K. C60 powder (99.9%)
was sublimated from a titanium crucible using an evaporation rate
of 2 ML/h, as calibrated by XPS. The background pressure during
evaporation was kept below 2 × 10−9 mbar. The ordered C60 chains
structure has been obtained by evaporating 1 ML of C60 onto the
surface held at 600 K. The quality of the film was confirmed by
the observation of a sharp (4 × 8 2 3 LEED pattern [8].

3. Results

C 1s core level spectra measured at different C60 coverage are
displayed in Fig. 2. The photon energy was 330 eV, the angle of
detection was normal to the surface and the angle of incidence of

![Fig. 1. Structural model for C60 exhibiting alternating chains of hexagon and pentagon bonded molecules, from [10]. The top view is along the [111] direction. The crossed markers show the different coordination to the copper atoms of the step for C60 of adjoining chains. The side view is along the [110] direction.](image)

![Fig. 2. C 1s XPS spectra of C60/Cu(553) measured at normal emission with increasing C60 coverage are displayed in Fig. 2. The photon energy was 330 eV, the angle of detection was normal to the surface and the angle of incidence of](image)
ponents, corresponding to C₆₀ molecules in the second layer and to 
from Tsuei et al. [26]. For a coverage over 1 ML there are two com-
confirmed by comparison of our valence band spectra with those 
from those from Tsuei et al. [26]. For a coverage over 1 ML there are two com-
ponents, corresponding to C₆₀ molecules in the second layer and to 
molecules interacting with the Cu(553) substrate, which appear at 
baning energies 285.2 eV and 284.7 eV, respectively. The compo-
ent due to the first layer is shifted by 0.5 eV towards lower bind-
ing energy, indicating screening by the substrate similar to that in 
Cu(110) and Cu(111) [26]. The full width at half maximum 
(FWHM) is 0.48 eV for the second layer component and 0.64 eV 
for the first layer component, slightly smaller than the FWHM for 
the first component on Cu(111), 0.73 eV.

For the higher coverage, two satellite peaks are clearly observed 
at 1.9 eV and 3.7 eV from the peak corresponding to the second C₆₀ 
layer. For bulk C₆₀, the shake-up structure contains six features, 
most of them assigned to transitions between molecular orbitals 
of the neutral states [26]. The peak that appears at 1.9 eV has been 
identified as an exciton from HOMO to LUMO derived states. Both 
satellite features are still visible for 1.3 ML C₆₀ but they are not 
present in the 0.9 ML film, which is consistent with the fact that 
chemisorption of the C₆₀ molecules in the first layer involves mix-
ing of the molecular and substrate levels in the initial and final 
states [27]. For 0.9 ML C₆₀, the C 1s peak displays an asymmetric 
line shape. This asymmetry has also been observed in 1 ML C₆₀ on 
Cu(111) and on Au(110) and it has been explained by a distribu-
tion of adsorption sites or by the metallic character of the over-
layer [24,26]. In our system the different orientations of the C₆₀ 
molecules in bright and dim chains could also cause a broadening 
due to the different coordination of the molecules in the two differ-
ent chains [10].

To precisely determine the resonance photon energy, the C 1s 
X-ray absorption spectrum was measured. The two curves shown 
in Fig. 3 correspond to 1.3 ML C₆₀ with the light polarization vector 
along and perpendicular to the C₆₀ chains. The light was grazing 
incident and the curves were normalized by the corresponding 
absorption curve measured in the clean substrate. As can be seen 
in the inset, the LUMO peak appears at an energy of 284.6 eV in 
the absorption curve measured with the polarization light vector 
perpendicular to the C₆₀ chains and at 284.8 eV when it is parallel 
to the chains. This decrease of energy in the LUMO absorption edge 
for the perpendicular geometry can be explained by hybridization 
of the corresponding LUMO orbitals with the steps.

Peaks corresponding to transitions to other π* levels appear at 
photon energies 286.5 eV and 288.45 eV. LUMO + 1 and LUMO + 2 
levels merge due to the interaction of the C₆₀ molecules with the 
substrate [26].

The features observed at 293 eV, 296.6 eV and 300.7 eV are due 
to transitions to σ states. At hv = 284.1 eV a step is clearly seen in 
the absorption spectra which is due to the onset of excitation from 
the C 1s level to the states above the Fermi level in the metallic 
substrate.

On the other hand, the energy of the LUMO peaks is very close 
to the core-level binding energy measured by XPS, indicating that 
the final states of the two processes are equivalent. This effect is 
characteristic of metallic overlayers and it is due to screening elec-
trons filling states at the Fermi level in the XPS process, which pro-
duces a final state identical to that of the NEXAFS lowest 
absorption [28]. In agreement with this, in a thick layer of 
C₆₀/Cu(111) the energy of the LUMO excitation is 0.7 eV lower 
than the binding energy of the C 1s XPS feature [26].

To study the charge transfer dynamics in C₆₀ chains, resonant 
photoemission measurements were performed with the polariza-
tion light vector parallel to the optical surface. The sample was ro-
tated azimuthally in order to place the electric field vector either 
parallel or perpendicular to the chains.

Fig. 4 shows the valence band photoemission spectra of 0.9 ML 
C₆₀/Cu(553) at the resonance energy with the polarization vector 
perpendicular (curve (b)) and parallel (curve (c)) to the C₆₀ chains. 
The photon energy was swept across the C 1s LUMO absorption 
edge in 0.2 eV steps. The expected resonance energy, hv = 284.7 ± 
0.1 eV, was determined by the LUMO peak position in the X-ray 
absorption spectra. As a reference, the resonance spectrum for 
1.7 ML C₆₀, measured with the polarization vector perpendicular 
to the chains, is shown in curve (a).

Features appearing at 2.3 eV, 2.75 eV and 3.5 eV correspond to 
the Cu 3d bands. The peak at 0.35 eV in curve (a) and around 
0 eV in curves (b) and (c) is due to C 1s 2nd order emission.

For 1.7 ML C₆₀, clear features corresponding to resonant photo-
emission from the HOMO, HOMO – 1 and HOMO – 2 levels 
appear at binding energies 1.76 eV, 3.28 eV and 5.5 eV, respec-
tively, for resonant photon energy 284.8 ± 0.25 eV. In the C₆₀ 
monolayer spectra (curves (b) and (c)) only the 3d bands from 
copper are visible when the photon energy is swept across the C 
1s absorption edge, between hv = 283 eV and hv = 285.5 eV. Small 
variations of those features between curves (a) and (b) are related 
to anisotropy of those Cu bands. There are no traces of resonance 
from the HOMO levels in curves (b) and (c). In effect, curve (d) 
resulting from the subtraction of curves (b) and (c) shows no dif-
ferences in the HOMO region between the two experimental 
geometries.

In the inset of Fig. 4, the contribution for photon energies out of 
resonance has been subtracted from the curves at resonance for 
1.7 ML and 0.9 ML C₆₀ with both orientations of the light. It can be 
seen that for 1.7 ML the HOMO, HOMO – 1 and HOMO – 2 res-
onant features become clearly visible, while for 0.9 ML those fea-
tures are not revealed by the subtraction. The photon energy was 
swept in an interval of 3 eV around the C 1s LUMO absorption 
edge and no HOMO features were either observed in the resulting 
subtractions.
4. Discussion

Resonant photoemission allows studying charge transfer events in the time-scale of the core-level relaxation time. In this technique, the photon energy is swept through the absorption edge of a given atomic species: here it is the carbon 1s edge. When the photon energy equals the energy difference between the C 1s and LUMO levels, an electron is excited from the C 1s to the LUMO. The relaxation can proceed through several radiative and non-radiative channels. In the so-called autoionization process or participant channel, an electron from the HOMO decays to the C 1s level and the electron from the LUMO is ejected. The final state of this process is the same as the one from the direct photoemission from the HOMO, which simultaneously takes place; an enhancement of the HOMO intensity is expected for the resonant photon energy [21]. The decay is also possible through ejection of an electron from deeper HOMO levels, so-called spectator channels. If the electron excited to the LUMO is transferred to another molecule or to the substrate, faster than the lifetime of the C 1s core-hole, it can not take part in the autoionization process and the decay proceeds through non resonant Auger emission.

To investigate the anisotropy of intermolecular hopping of the LUMO, we have evaluated the dependence of the resonant photoemission features on the direction of the electric field vector. The LUMO orbital of C60 is mainly derived of combinations of π orbitals with radial orientation. Thus, when the polarization vector is parallel to the surface, the C 1s-to-LUMO excitation probability is enhanced for the orbitals with axes parallel to the surface. When the light vector is perpendicular to the surface, the excitation to orbitals with axes perpendicular to the surface is favored. This has been demonstrated for C60/Al(1 1 0) [25].

Similarly, it should be possible to enhance charge transfer either along or parallel to C60 chains by tuning the light vector in those directions. However, in our experimental data of Fig. 4 it can be seen that for 0.9 ML C60/Cu(5 5 3) no HOMO resonance is observed, indicating a complete delocalization of the excited electron on the LUMO, on the femtosecond time-scale. Only features corresponding to second order C 1s and the Cu d bands are seen in curves (b) and (c), independently of the orientation of the light polarization vector.

The intermolecular hopping for an electron excited to the LUMO in solid C60 has been shown to be negligible due to electron correlations, which localize the excited state to the probed molecule [29]. For C60 chains, the 400 meV dispersion measured for the HOMO by ARPES indicates strong intermolecular coupling along the chains. On the other hand, the C60–C60 distance in the perpendicular direction is 4% larger than along the chains [8] and than in solid C60. As the hopping between C60–C60 π orbitals is very sensitive to the distance between the molecules, the C60 band dispersion is smaller along the perpendicular direction [10].

Therefore, in order to explain the delocalization of the excited electron found in both cases, the C60–substrate interaction must be taken into account, and it appears to be stronger than the molecule–molecule hybridization. As shown in the previous section,
XPS and NEXAFS data are consistent with a strong C60–substrate interaction, affecting the electronic structure. In particular it was noticed that very efficient screening from the substrate causes similar final states for the C 1s → LUMO NEXAFS and C 1s XPS processes [28]. In those conditions, the autoionization becomes equivalent to Auger decay and the HOMO resonance is not expected anymore. The lack of a visible resonance can be interpreted, similarly to C60/Au(110), as the signature of hybridization between the core-hole perturbed t2g orbital and the Cu(553) sp band, with bonding interaction larger than the lifetime of the C 1s, around 0.1 eV [24,25]. ARPES data from the parent system C60/Cu(111) are in line with the present results. In that case the strong hybridization at the C60/metal interface significantly modifies the electronic structure of the molecular layer, causing the appearance of an extra dispersing peak within the HOMO–LUMO gap [30]. Compared to C60 monolayers on other noble metals, our results indicate that the interaction of C60 with Cu(553) is stronger than for Au(110) [24] and the vicinals Ag(554) and Au(443), for which some intensity is still detected at the HOMO resonance. In the case of C60/Al, although the chemical bond to the substrate is predominantly covalent [31], the HOMO resonance has been clearly observed in the ML system. This suggests us that the short lifetime of the excited state in C60/Cu(553) is not only due to the strength of the bonding but also to the specific C60/metal electronic structure.

From our experimental data, it can also be inferred that for C60/Cu(553) it is not possible to localize the core-hole in a particular region of the C60 molecule by selecting the direction of the electric vector. Some degree of localization for electrons excited to the LUMO in C atoms from the sides of the molecule, which are not in contact with the substrate, could have been expected. As a test, we also performed resonant photoemission with the electric vector perpendicular to the surface, which should locate a hole on the top part of the molecule (data not shown). However in all cases we found no traces of HOMO resonance, meaning that the hybridization with the substrate affects the whole C60 molecule, in contrast with results on C60/Al(111) and Al(110) [25]. On the other hand, the second C60 layer is much less affected by hybridization to the substrate, as demonstrated by the presence of the HOMO participator and spectator features in the curve (a) of Fig. 4.

5. Summary

In conclusion, our resonant photoemission study of C60 monolayers on Cu(553) shows that the excited electron delocalizes on a time-scale faster than the C 1s lifetime, probably due to hybridization of the LUMO orbital with the substrate. Consistently, NEXAFS and XPS data show signs of strong molecule–substrate interaction. The core-hole weight appears to be distributed in all the molecule and isotropic charge transfer to the substrate is observed.

References