Charge-transfer dynamics in one-dimensional C_{60} chains

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ABSTRACT

Charge transfer in highly-ordered C_{60} chains grown on a Cu(553) vicinal surface is studied by means of resonant photoemission. Tuning the light polarization, autoionization of the highest occupied molecular orbital (HOMO) was expected to detect anisotropy in this one-dimensional system. For one monolayer C_{60} we found no signature of autoionization. This indicates that for an electron which is excited from the C 1s level of C_{60} to the lowest unoccupied molecular orbital (LUMO), hybridization leads to delocalization on the femtosecond time-scale and no influence of the light polarization is observed.

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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 terrace and step sizes for a given molecule can be selected in the nanometric scale by tuning the miscut angle. As a result of the combined effect of molecule–molecule and molecule–substrate interactions, single molecular chains can be grown along the step edge. This approach has given very good results for the formation of ordered one-dimensional C_{60} chains on metal surfaces [8,9].

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 alkali 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_3C_{60} layer on Ag(111) [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
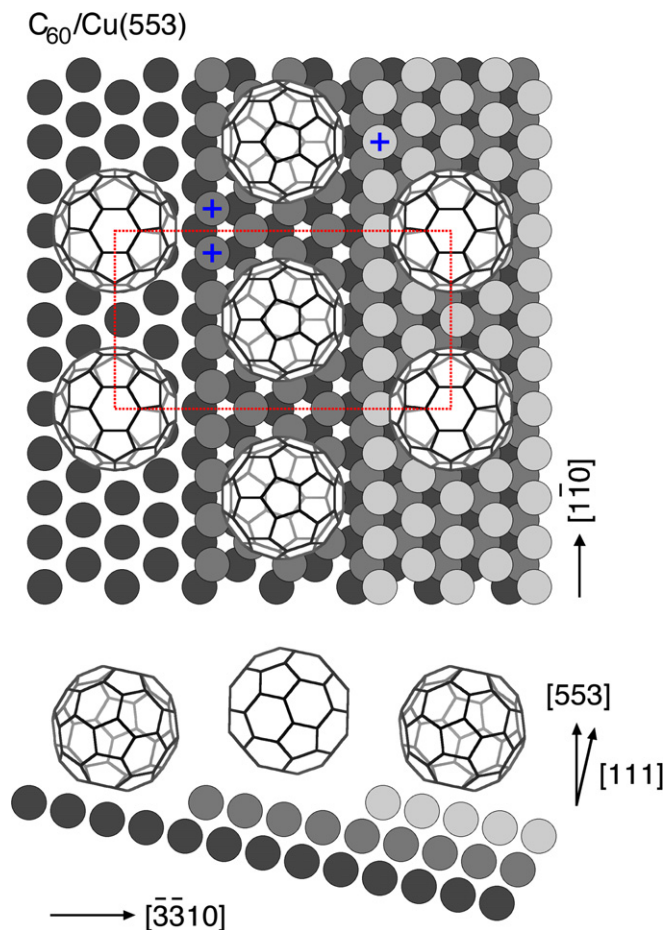
C$_{60}$/Cu(553)

Fig. 1. Structural model for C$_{60}$ exhibiting alternating chains of hexagon and pentagon bonded molecules, from [10]. The top view is along the [1 1 1] direction. The crossed markers show the different coordination to the copper atoms of the step for C$_{60}$ of adjoining chains. The side view is along the [1 $\bar{1}$ 0] direction.

is very different from the typical LUMO spectra for two-dimensional C$_{60}$ 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 molecule–substrate electron hopping mechanism, we investigated the C$_{60}$ chains by resonant photoemission, also referred to as autoionization [21–23]. From the decay process of an electron excited from a core level to the LUMO it is possible to deduce the electron hopping 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 participant channel is quenched. With this technique, Maxwell et al. proved the hybridization of the core-hole perturbed C$_{60}$ orbitals and the sp band of the metal substrate in C$_{60}$/Au(1 1 0) [24]. The directional character of the π^* orbitals that form the LUMO in C$_{60}$ allows tuning the excitation to different parts of the C$_{60}$ molecule by selecting the direction of the light polarization vector, as demonstrated by Maxwell et al. for C$_{60}$/Al(1 1 0) [25]. We take advantage of this fact as a complementary method to investigate possible anisotropy in the LUMO derived intermolecular interactions in the directions parallel and perpendicular to the C$_{60}$ chains. Our results show that in the case of 0.9 ML C$_{60}$/Cu(5 5 3) the anisotropic 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 performed at the surface and interface spectroscopy (SIS) beamline at the Swiss Light Source, Paul Scherrer Institut (Villigen, Switzerland). 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 resolution 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 $3p_{3/2}$ core level measured in the clean Cu substrate and the Cu Fermi level measured at the same photon energy, $hv = 275$ eV. All the data were acquired at room temperature (RT) and the pressure during the measurements remained below 2×10^{-10} mbar.

Cu(5 5 3), the stepped surface used in this work, is a B-type vicinal of Cu(1 1 1) with a miscut angle of 12.3°. It is composed of (1 1 1) terraces separated by monoatomic steps with (1 1 $\bar{1}$) step facets. The nominal terrace width is 9.8 Å, which is close to the van der Waals diameter of the C$_{60}$ molecule. The Cu(5 5 3) single crystal was cleaned by several cycles of argon ion sputtering at 1000 V and 700 V and annealing at 700 K. C$_{60}$ 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 C$_{60}$ chains structure has been obtained by evaporating 1 ML of C$_{60}$ onto the surface held at 600 K. The quality of the film was confirmed by the observation of a sharp $(4 \times 8\frac{2}{3})$ LEED pattern [8].

3. Results

C 1s core level spectra measured at different C$_{60}$ 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
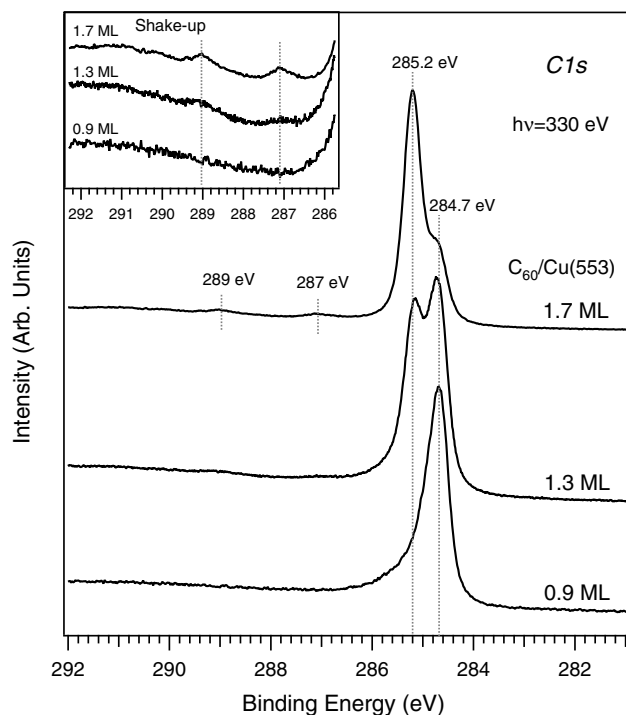

Fig. 2. C 1s XPS spectra of C$_{60}$/Cu(5 5 3) measured at normal emission with increasing C$_{60}$ coverage. The contribution corresponding to molecules in the first layer is shifted towards lower binding energy due to screening from the substrate. A zoom of the satellite region can be seen in the inset at the upper left corner.