

Charge transfer of 1 ML C₆₀/Ag(100)^{*}

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Abstract We have measured the synchrotron radiation photoelectron spectra of monolayer C₆₀ on Ag(100). By calculating the intensity ratios between the LUMO bands and the two deeper bands (HOMO and HOMO-1), we estimate the amount of the charges transferred from Ag(100) to C₆₀ within the range of 1 e to 1.8 e. The results dismay the expectation of surface superconductivity and afford a good reference for further studies of the monolayer C₆₀/Ag(100) system.

Key words 1 ML C₆₀/Ag(100), charge transfer, photoelectron spectroscopy

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1 Introduction

C₆₀ monolayer on various metal surfaces has attracted much attention in recent years due to its fundamental interest and possible technological applications^[1–3]. A C₆₀ monolayer on Ag(001) surface (denoted as 1 ML C₆₀/Ag(001) in the following) is a very interesting system among monolayer systems. With successive endeavors in the past decade, especially the scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) studies^[4–10], the geometric structure of 1 ML C₆₀/Ag(001) has been understood in detail. The C₆₀ monolayer is highly inhomogeneous and aperiodic. About 37 percent of the C₆₀ molecules (the so-called B molecules in the literature^[4–10]) are adsorbed on the nonreconstructed region of the Ag(100) surface, while about 63 percent of the molecules (the so-called D molecules) sit in pits^[10]. The pits are the reconstructed region of the Ag(100) surface induced by C₆₀ adsorption, and each pit is formed with four Ag atoms removed from the topmost substrate layer and (possibly) one Ag atom from the second layer. The D molecules can be further classified into two groups (DM and DD^[10]) with the number ratio near 1:1.

On the electronic structure side, it is believed that nearly three (2.7) electrons are transferred from the Ag(100) to the lowest-unoccupied-molecular-orbital (LUMO) derived band of each C₆₀ molecule according to the electron energy loss spectroscopy (EELS) and photoelectron spectroscopy (PES) studies^[11, 12]. This rather large amount of charge transfer indicates that the bonding nature of the C₆₀-Ag interface should be predominantly ionic^[11, 12]. More interestingly, the charge transfer of 2.7 e from Ag to C₆₀ is nearly the same as that (3 e) from K or Rb to C₆₀ in the superconducting A₃C₆₀ (A=K, Rb) fullerenes, and stimulates the researching work aiming at the surface superconductivity^[13]. However, the energy gap opening below ~250 K (indication of superconducting transition) observed in the PES measurements by Cepek et al^[13] has not been confirmed by other groups with either PES^[14] or STS^[6] measurements. What is more, some recently published works^[9, 10] reported much small amount of the charge transfer (~0.2 e) by ab initio pseudopotential density functional calculations. Therefore more work is needed to address the topic of the charge transfer in order to get the precious knowledge about the electronic structure of 1 ML C₆₀/Ag(001).

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In this paper, we will report the synchrotron radiation photoelectron spectroscopy (SRPES) study of 1 ML C₆₀/Ag(001) within the photon energy range from 21.2 eV to 41.2 eV. The amount of the charge transfer is quantitatively determined from the spectral intensities of the LUMO band, the highest-occupied-molecular-orbital (HOMO) derived band, and the HOMO-1 band of the spectrum recorded with the photon energy of 21.2 eV. Our conclusion is that the amount of the charge transfer falls in the range from 1 e to 1.8 e, which is drastically different from that reported previously^[9–12]. The reason for the discrepancy is discussed, and we believe our result is more reliable.

2 Experiment

Sample preparation and measurements were performed at the Photoelectron Spectroscopy Station of Beijing Synchrotron Radiation Facility (BSRF). The base pressure of the experimental system was 4×10^{-10} mbar. An angle-resolved energy analyzer was used to record the photoelectrons at normal emission. The total energy resolution was ~ 0.1 eV with the incident photon energy around 21.0 eV and got slightly worse with higher photon energy. The spectra were measured with different photon energies ranging from 21.2 eV to 41.2 eV.

The Ag single crystal was cleaned by cycles of 1 keV Ar⁺ bombardment and annealing at $\sim 550^\circ\text{C}$ until the C 1s and O 1s signals could not be observed by the X-ray photoemission (XPS) measurement. The morphology of the clean single crystal, as checked with STM measurement^[10], exhibited large terraces with the widths greater than 100 nm. Thoroughly degassed C₆₀ was sublimed from a Ta boat located at about 11 cm from the Ag(100) substrate.

The amount of C₆₀ deposited on the substrate was controlled by the electric current through the Ta boat and deposition time. During deposition, the substrate was kept at room temperature. We first deposited ~ 4 ML C₆₀ on the Ag(100), and then gradually annealed the sample to 300°C to evaporate the C₆₀ multilayer (C₆₀ film begin to evaporate at 180°C in the ultra-high-vacuum environment^[15], but the monolayer of C₆₀ molecules in direct contact with the Ag atoms will stay on the surface below 475°C ^[12]). After staying at 300°C for 20 minutes, the sample was cooled down to room temperature and transferred from the preparation chamber to the analyzer chamber for SRPES measurements.

3 Results and discussion

Figure 1 shows the SR-PES results of 1 ML C₆₀/Ag(100). The photon energies are indicated next to the lines. The spectral lines of ~ 4 ML C₆₀ and the clean Ag(100) substrate are also exhibited as the dashed and dotted lines for comparison. All the lines have been normalized to the incident photon flux, and the bottom two lines have been further multiplied by proper coefficients to fit the figure scale. Compared with the multilayer C₆₀, 1 ML C₆₀/Ag(100) exhibits some spectral weight between the Fermi level (E_f) and ~ 1.3 eV. This is the LUMO band that is partially filled due to the charge transferred from Ag to C₆₀, together with some contribution from the substrate. The filling of the LUMO band and the (possible) screening effect of the metal substrate also affect the energy positions of other bands. For examples, the HOMO and HOMO-1 bands of 1 ML C₆₀/Ag(100) shift to lower binding energy by ~ 0.45 eV. The Ag(100) has a strong Ag 4d photoemission between 3.5 eV and 7.5 eV, and the spectral feature around 4.3 eV is from the surface resonance state^[16]. The spectral weight between the Fermi level and 3.5 eV of the substrate is from the Ag 5sp valence band.

The substrate has non-negligible contribution to the spectra of 1 ML C₆₀/Ag (100). The 21.2 eV spectrum of 1 ML C₆₀/Ag (100) exhibits a shoulder around 4.3 eV, which was also observed by other groups^[12]. With the increased photon energies, the shoulder becomes stronger, and the line shape around 5.4 eV (the HOMO-2 band) changes significantly. Above the photon energy of 25 eV, a sharp feature locating at ~ 5.0 eV dominates the HOMO-2 band. The three vertical dash-dotted lines in Fig. 1 reveal that the above observations are due to the substrate contribution. The photoionization cross-section of Ag 4d increases, while the cross-section of C 2p decreases with the increase of photon energy within the energy region of Fig. 1^[17]. Therefore the substrate contribution is more significant at higher photon energies. By the way, the positions of the spectral peaks of Ag 4d seem invariant before and after C₆₀ adsorption.

The substrate contribution to the experimental data of 1 ML C₆₀/Ag (100) must be properly subtracted to obtain the intensities of the LUMO, HOMO and HOMO-1 bands, which is a very difficult task as will be discussed below. Another difficulty in determining the amount of the charge transfer is the photoionization cross-section oscillations^[18, 19] of the valence bands of C₆₀. All the LUMO, HOMO

and HOMO-1 orbitals are C 2*p* states. If the cross-sections of these bands are the same as C 2*p*, the intensity ratios between these bands should not change with photon energy, and they should be equal to the number ratios of the occupied electrons. For example, the ratio should be 10/18 between the five-fold degenerated HOMO and the nine-fold degenerated HOMO-1. However, it is not the case, the cross-sections oscillate with photon energy due to the final state effect and the interference between the photoelectron waves^[18, 19]. Accordingly, one can't yet determine the amount of the charge transfer even with accurate intensity data of the LUMO, HOMO and HOMO-1 bands. Fortunately, we^[20] previously reported a spectrum of Rb₃C₆₀ (Line 13 in Fig. 1 of Ref. [20]) recorded with the photon energy of 21.0 eV, and

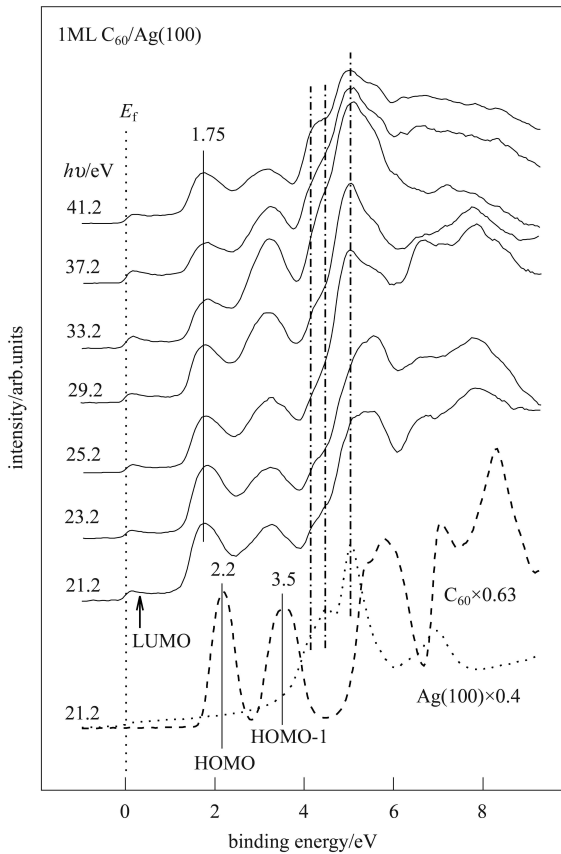


Fig. 1. SR-PES of 1 ML C₆₀/Ag(100) recorded at normal emission. The incident photon energies are indicated next to the lines. The spectra of ~ 4 ML C₆₀ and the clean Ag(100) are also shown for comparison, as represented by the dashed and dotted lines, respectively. For Ag(100), the spectral weight from ~ 3.5 eV to ~ 6.5 eV is derived from the 4*d* band, and the photoemission between the Fermi level and ~ 3.5 eV originates from the Ag 5*sp* band. All the lines are normalized to the incident photon flux.

calculated the intensity ratio (10%) between the LUMO band and the combined HOMO and HOMO-1 bands. This ratio of 10% can be used as a reference of three electrons transferred to C₆₀ in analyzing the spectra recorded with the photon energies very close to 21.0 eV, such as the 21.2 eV spectrum in Fig. 1. In the following, we quantitatively analyzed the 21.2 eV spectrum to deduce the amount of charge transfer.

We carried out two different data processing procedures to estimate the low and high thresholds of the amount of charge transfer, respectively. Fig. 2 schematically shows the procedure of determining the low threshold. According to the discussion of Fig. 1, the kink around 4.3 eV of the spectrum recorded with the photon energy of 21.2 eV is due to the contribution of the surface resonant state of the substrate (or the interface state after C₆₀ adsorption). Fig. 2(a) normalizes the spectrum of the clean Ag(100) (dotted line) to the spectral height at 4.3 eV of the spectrum of the 1 ML C₆₀/Ag (100) (filled circles). Then we subtracted the two spectral lines, and obtained the solid line (vertically shifted for clarity) that approximately represents the spectrum (from the Fermi level to the HOMO-1 band) of the 1 ML C₆₀/Ag (100) with no substrate contribution. This data processing obviously overestimates the substrate contribution, and the obtained intensity (area) of the LUMO band is only about half of the original intensity. Therefore the amount of charge transfer determined in the following (Fig. 2(b)) should be the low threshold of charge transfer. Fig. 2(b) determines the intensities of the LUMO band and the combined HOMO and HOMO-1 bands based on the solid line in Fig. 2(a) (redrawn in Fig. 2(b) with the bold solid line). We simulated the HOMO and HOMO-1 bands with two and three Gaussian functions respectively. The sum of the five Gaussian functions constitutes the combined HOMO and HOMO-1 bands, as indicated in the figure with the dashed line. The LUMO band is then obtained by subtracting the bold solid line with the dashed line, as represented by the dotted line. Please note that the dashed and dotted lines in Fig. 2(b) are vertically shifted for clarity. The intensities of the LUMO band and the combined HOMO and HOMO-1 bands thus determined are 201.0 and 5837.1, respectively. Their intensity ratio is 0.0344 (=201.0/5837.1). Comparing with the ratio of 0.1 for Rb₃C₆₀^[20], we obtained the low threshold of the charge transfer which is 1.032 e for 1 ML C₆₀/Ag (100).

To estimate the high threshold of the amount of charge transfer, we assume that the observed spectrum is entirely the photoemission of the C₆₀ mono-

layer, i.e., the contribution of the substrate is ignored. Fig. 3 exhibits the quantitative determination of the spectral intensities. We simulated the part region from 1.3 eV to 4.1 eV (indicated with two short vertical arrows) of the spectrum of the 1 ML C₆₀/Ag(100) (filled circles) with five Gaussian functions and an exponential function. The start point (1.3 eV) is selected to avoid the LUMO contribution, and the exponential function is used to simulate the overlapping of the HOMO-1 band and the adjacent deeper bands. The bold solid line superimposed on the filled circles is the simulated result, which indicates our simula-

tion is fairly well. The sum of the five Gaussian functions constitutes the combined HOMO and HOMO-1 bands, as indicated in the figure with the dashed line. By subtracting the filled circles with the dashed line, we obtained the LUMO band as represented by the dotted line. Also, the simulated LUMO, HOMO and HOMO-1 bands are vertically shifted for clarity. The intensities of the LUMO band and the combined HOMO and HOMO-1 bands determined in Fig. 3 are 423.6 and 7151.8, respectively. Their intensity ratio is 0.0592. We thus obtained the high threshold of the charge transfer which is 1.776 e.

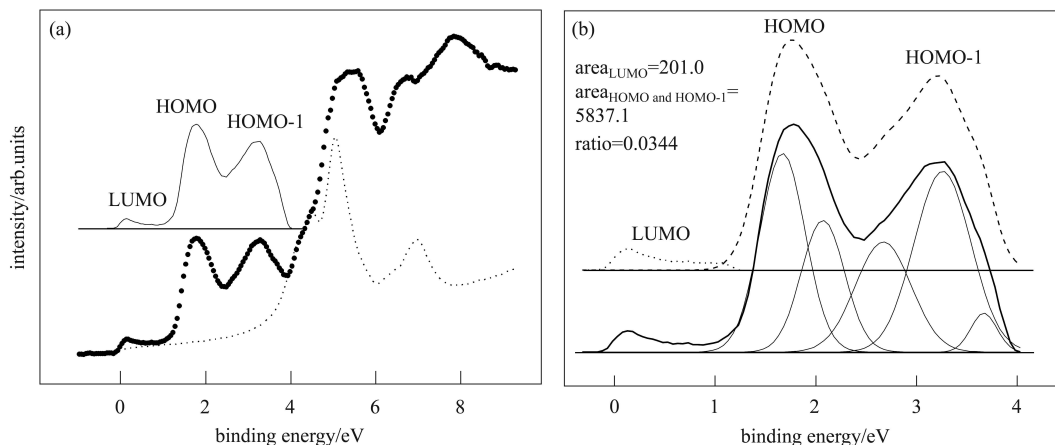


Fig. 2. Determination of the low threshold of the amount of the charge transfer for 1 ML C₆₀/Ag (100). See the text for more detail.

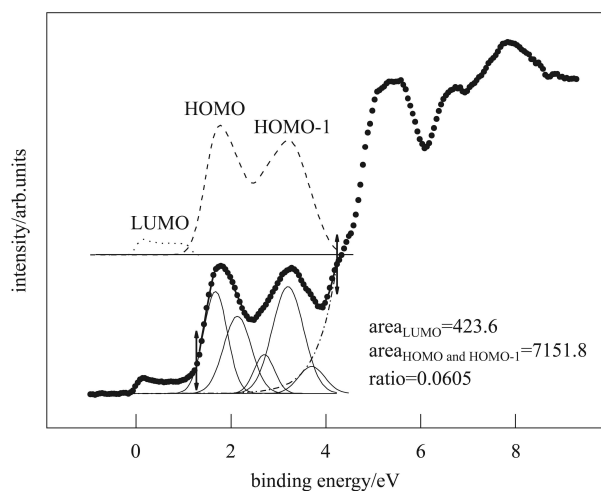


Fig. 3. Determination of the high threshold of the amount of the charge transfer for 1 ML C₆₀/Ag (100). See the text for more detail.

We have tried to estimate more accurate datum of the amount of charge transfer. This required proper and reliable subtraction of the substrate contribution as done for 1 ML C₆₀/Ag (111)^[21], but we failed.

This case is due to the fact that the spectral feature locating around 4.3 eV of Ag(100) is the surface resonant state (or interface state) that is sensitive to adsorption. The surface resonant state does not disappear in Fig. 1, but certainly changes its spectral shape and intensity drastically after the C₆₀ adsorption. Therefore the spectrum of the clean Ag(100), multiplied by whatever coefficient to adjust its relative intensity with respect to the spectrum of the 1 ML C₆₀/Ag(100), is strictly not the photoemission of the substrate. Indeed, we failed to obtain a reasonable spectrum of the C₆₀ monolayer (with the spectral shape between ~4.0 eV and 9.0 eV not too different from that of the 4 ML C₆₀) by adjusting the relative intensity and even shifting the peak positions (binding energies) of the spectrum of Ag(100).

We have done our best to estimate the amount of charge transfer for 1 ML C₆₀/Ag (100). The conclusion is that the number of electrons transferred from Ag to C₆₀ is within the range of 1.0 e to 1.8 e. Though this result has a rather large span, it is still distinctly different from that reported previously^[9–12]. The

2.7 e charge transfer^[11, 12] was deduced from a EELS study, which is an indirect method to charge transfer. The calculated results of ~ 0.2 e charge transfer^[9, 10] are obviously too small to interpret the PES data of the present work and much other work. The calculations are based on the simulations of the adsorption system by a C₆₀ molecule and a supercell containing 200 surface atoms and four atomic layers of Ag^[9], or a repeated-slab geometry consisting of one layer of C₆₀, four layers of Ag, and a 1 nm vacuum spacer^[10]. We argue the bulk properties, such as the work function of Ag(100), are also crucial factors to determine the charge transfer, besides the interaction at the interface. The substantial discrepancy between the calculated results and the PES data may be due to the fact that the calculations^[9, 10] could not describe the bulk property, though they could describe the interface fairly well. In contrast, our method of determining the amount of the charge transfer by the PES intensities is the most direct and reliable method. Al-

though there should be some uncertainties of our result due to the procedures of the curve fitting and the negligence of the effect of some covalent contribution to the C₆₀-Ag bonding at the interface on the spectral intensities, we believe it is beyond doubt that the exact amount of the charge transfer falls in the range of 1.0 e to 1.8 e.

4 Conclusions

The amount of the charge transferred from Ag(100) to C₆₀ monolayer is within the range of one electron to 1.8 electrons per molecule, which should be the foundation for further studies of the electronic structure for 1 ML C₆₀/Ag(100). The result is far from the three electrons of the charge transfer for superconducting A₃C₆₀, and we thus can not expect a surface superconductor for 1 ML C₆₀/Ag(100) based on the amount of charge transfer.

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