Spatially resolved conductance of oriented C$_{60}$

G Schull$^1$, N Néel, M Becker, J Kröger and R Berndt

Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany
E-mail: schull@physik.uni-kiel.de

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Abstract. The conductance of oriented C$_{60}$ molecules on Au(111) and Cu(100) was investigated using a low-temperature scanning tunnelling microscope. A remarkable dependence of spectra of the differential conductance on the adsorption orientation is observed for Au(111) that is almost absent for Cu(100). For C$_{60}$ adsorbed on Au(111), the spatial distribution of the three lowest unoccupied molecular orbitals is revealed by maps of the differential conductance.

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1. Introduction

The C$_{60}$ molecule has become the basic structural unit of a variety of carbon materials. In addition to the wealth of C$_{60}$-based structures, these materials exhibit intriguing electronic properties which have been addressed by, for instance, spatially averaging techniques like photoemission and inverse photoemission [1]–[3]. While these techniques provide a general trend of charge transfer between C$_{60}$ and a noble metal surface, the investigation of the local electronic structure of an individual molecule requires spatial resolution down to

$^1$ Author to whom any correspondence should be addressed.
the atomic scale together with high energy resolution for occupied as well as unoccupied states. Therefore, scanning tunnelling microscopy (STM) and spectroscopy experiments have been performed on C\textsubscript{60} on various surfaces (see, for instance, [4] and references therein). These studies have shown that different adsorption geometries—orientation and adsorption site—as well as intermolecular interactions affect the C\textsubscript{60} electronic properties [5]–[7]. However, the respective roles of these parameters have not been disentangled and no direct relation between a single parameter and the electronic structure of individual molecules has been reported for C\textsubscript{60} adsorbed on noble metal surfaces.

In this paper, we report the first experimental evidence of the influence of the C\textsubscript{60} orientation, independently of the other adsorption parameters, on the electronic properties of C\textsubscript{60} molecules. In particular, using Au(111) and Cu(100) as drastically different adsorption platforms we observed a clear dependence of dI/dV spectra on the C\textsubscript{60} orientation on Au(111), while on Cu(100) the molecular electronic structure appears to be rather independent of the orientation. We argue that this effect may be due to the different reactivities of these surfaces and we thus tentatively relate the degree of orientation dependence to the amount of charge transfer between the substrate and molecule.

2. Experiment

The experiments were performed with low-temperature scanning tunnelling microscopes operated at 5.7 and 7.5 K in ultrahigh vacuum with base pressures below 10\textsuperscript{−9} Pa. Au(111) and Cu(100) surfaces as well as chemically etched W tips were prepared by argon-ion bombardment and annealing. C\textsubscript{60} was deposited from a tantalum crucible at a rate of \(\approx 1\) ML min\textsuperscript{−1} as monitored by a quartz microbalance. One monolayer (ML) corresponds to C\textsubscript{60} densities of 1.16 and 1.15 nm\textsuperscript{−2} for Au(111) and Cu(100), respectively. During deposition a residual gas pressure in the \(5 \times 10\textsuperscript{−8}\) Pa range was maintained and the sample was kept at room temperature. Ordered domains of C\textsubscript{60} on Cu(100) were obtained by subsequent annealing at around 500 K. The data shown correspond to coverages of \(\approx 0.2\) ML. All images were recorded in a constant-current mode with the voltage \(V\) applied to the sample. For detection of the differential conductance, dI/dV, we applied standard lock-in techniques. Maps of dI/dV were recorded simultaneously with constant-current STM images [8].

3. Results and discussion

At room temperature, sub-monolayer amounts of C\textsubscript{60} deposited on noble metal surfaces aggregate and form molecular clusters of monolayer height. On Au(111), the three C\textsubscript{60} superstructures, \((2\sqrt{3} \times 2\sqrt{3})R30^\circ\), \((7 \times 7)\) [6, 9, 10], and the orientationally ordered \((\sqrt{589} \times \sqrt{589})R14.5^\circ\) [11], have been observed. Figure 1(a) is an STM image of C\textsubscript{60} molecules self-organized in the thermodynamically stable [12] and commensurate \((2\sqrt{3} \times 2\sqrt{3})R30^\circ\) structure. In this superstructure molecules occupy equivalent positions with respect to the substrate lattice [10, 11, 13].

The two adsorption orientations of C\textsubscript{60} on Au(111) can be clearly distinguished by the intramolecular pattern exposed to vacuum (labelled 1 and 2 in figure 1(a) and shown as a close-up view in figure 1(b)). Orientation 1 corresponds to C\textsubscript{60} adsorbed on a hexagon, while orientation 2 corresponds to C\textsubscript{60} adsorbed on a double bond between two adjacent hexagons.
Figure 1. (a) 5.5 × 5.5 nm² and (b) 1.8 × 1.2 nm² STM images (sample voltage \( V = 0.5 \) V, tunnelling current \( I = 1 \) nA of \( (2\sqrt{3} \times 2\sqrt{3})R30° \) \( C_60 \) islands on Au(111). While the molecules were deposited at ambient temperature images were recorded at 5 K. (c) Top view model of the lateral arrangement of the molecules. Au: small grey circles, \( C_60 \): large black circles. Only bottom halves of \( C_60 \) are represented in order to expose the relative atomic positions at the interface.

(6 : 6 bond) [14]. These adsorption configurations necessarily lead to two different molecule–substrate interfaces. Recent calculations suggest that the most stable configuration is \( C_60 \) adsorbed with a hexagon (type 1) facing a hexagonally close-packed (hcp) site of Au(111) [15]. Considering this absolute position for type 1 molecules, the adsorbed configuration of type 2 molecules can also be inferred (figure 1(c)). Both configurations occur with similar frequency and, in contrast to the \( (\sqrt{5}89 \times \sqrt{5}89)R14.5° \) structure [11], no obvious orientational order is found. We note that the above data are the first to display detailed submolecular resolution of \( C_60 \) in the \( (2\sqrt{3} \times 2\sqrt{3})R30° \) superstructure. The molecular orientations we propose are different from those inferred previously [9].

Spectra of \( dI/dV \) taken on the top of the molecules are presented in figure 2(a). The red (blue) curve corresponds to spectra obtained on type 1 (2) molecules. The spectra recorded from molecules with identical orientations did not depend on orientations of the nearest neighbour molecules. The assignment of the HOMO, LUMO, LUMO + 1, and LUMO + 2 to spectral signatures shown in figure 2(a) is based on published results [7, 16]. The orbital energies of both \( C_60 \) types are summarized in table 1. The unoccupied states of type 1 \( C_60 \) are slightly shifted towards the Fermi level compared with type 2. This effect is more clearly discernible in the close-up view presented in figure 3(a) (upper graph).

The spectra of figure 2 were measured at a single position over the molecule which implies the possibility that the observed shift may be due to small differences in lateral tip position. Indeed, the interaction with the metal surface lifts the degeneracy of the orbitals of the free
Figure 2. (a) $dI/dV$ spectra from tip positions centered above C$_{60}$ molecules adsorbed on Au(111) in two different orientations (type 1 and type 2). To cover the fairly wide voltage range, the spectra were recorded stepwise with the feedback loop opened at ($V = 3.6$ V; $I = 1$ nA), ($V = 2.5$ V; $I = 1$ nA) and ($V = -2.5$ V; $I = 1$ nA). (b) $5.5 \times 5.5$ nm$^2$ $dI/dV$-maps ($I = 1$ nA) from the surface area of figure 1(a) showing the LUMO (0.6 V), LUMO + 1 (1.9 V) and LUMO + 2 (3.1 V). Blue (red) circles indicate a single type 1 (2) molecule. A more detailed animated sequence of $dI/dV$ maps measured at 100 mV intervals is available from stacks.iop.org/NJP/10/065012/mmedia.

Table 1. Orbital energies (in eV relative to the Fermi energy) of C$_{60}$ measured by STS for different noble metal surfaces and adsorption configurations. Data for C$_{60}$ monolayer (ML) on Ag(100) and for individual C$_{60}$ on Au(111) are taken from [4].

| Surface   | Monomer | Type 1 | Type 2 | Bright | Dim | All types |
|-----------|---------|--------|--------|--------|-----|-----------|
| Au(111)   | -1.7    | -1.8   | -1.8   | -1.8   | -1.8| -1.9      |
| Au(111)   | 1.0     | 0.7    | 0.84   | 0.55   | 0.49| 0.43      |
| Ag(100)   | 2.2     | 2.01   | 2.08   | 1.75   | 1.62| 1.71      |
| Cu(100)   | -       | 3.08   | 3.13   | -      | -   | -         |
Figure 3. (a) Constant-height d$I$/d$V$ spectra obtained above the centres of both C$_{60}$ orientations on Au(111) (upper spectrum) compared to constant-current spectra averaged over small areas (coloured circles of 0.2 nm$^2$ added to the STM image displayed in inset) chosen at the centre of the same molecules. All constant-current spectra have been generated from a sequence of d$I$/d$V$ maps (see supplementary material available from stacks.iop.org/NJP/10/065012/mmedia). Constant-current d$I$/d$V$ spectra averaged over different areas ((b) 0.2 nm$^2$ and (c) 1 nm$^2$) of both C$_{60}$ types.

molecule and may result in spatial inhomogeneity of the orbitals over the molecule [17]. To further explore this possibility, we use maps of the differential conductance at different voltages, which provide information on the spatial distribution of molecular orbitals.

A sequence of d$I$/d$V$ maps recorded between 0.5 and 3.5 V in steps of 0.1 V is included in the supplementary material (available from stacks.iop.org/NJP/10/065012/mmedia). From these data, d$I$/d$V$ spectra have been generated by lateral averaging over a given molecule. Since the distance between the tip and the sample varies with voltage, the spectra may approximately be considered as constant-current d$I$/d$V$ spectra which implies a shift of spectral peaks towards the Fermi energy compared to constant-height data\(^2\). The lower graph in figure 3(a)

\(^2\) A detailed analysis of these shifts is currently in progress [18].
shows constant-current spectra of type 1 and 2 molecules averaged over areas of 0.2 nm$^2$ at the centres of the molecular patterns. Similarly to constant-height spectra (upper graph in figure 3(a)), a shift of $\approx 100$ mV of the LUMO + 1 maximum is measured in between both orientations, confirming that both spectroscopic methods lead to equivalent results. The spatial inhomogeneity of the LUMO + 1 orbital is illustrated in figure 3(b) where spectra averaged over different submolecular areas show LUMO + 1-related peaks at different energies. To obtain a spectrum characteristic for a given orientation, averaging over the full area corresponding to one molecule was used. These averaged spectra are displayed in figure 3(c) for both orientations. A shift of $\approx 250$ mV of the LUMO + 1 maximum is clearly discernible. Due to the limited voltage range probed in this experiment, no definitive statement is possible about shifts of the LUMO and LUMO + 2 peaks.

Figure 2(b) displays $dI/dV$ maps recorded at voltages corresponding to the LUMO, LUMO + 1, and, for the first time, LUMO + 2 and thus reflect the spatial distribution of the respective orbitals. At these voltages, sharp features are obtained whereas the maps appear blurry at minima of the $dI/dV$ spectra. As reported previously, a contrast inversion between LUMO and LUMO + 1 is observed $[17]$. The pattern observed for LUMO+2 resembles the characteristic pattern of the LUMO.

We now discuss C$_{60}$ on Cu(100) where bonding strength and charge transfer are larger than on Au(111). On Cu(100) (figure 4) C$_{60}$ aggregates in a pseudo-hexagonal lattice which exhibits an alternation of bright and dim rows. This superstructure has been attributed to a missing-row reconstruction of the Cu substrate $[19]$. Bright molecules are adsorbed in missing Cu rows, dim molecules are located in double missing rows. Submolecular resolution enables identification of

**Figure 4.** (a) A 4.5 × 4.5 nm$^2$ constant-current image (left) ($V = 1.7$ V and $I = 1$ nA) of C$_{60}$ on Cu(100) and related adsorption model (right). (b) $dI/dV$ spectra recorded above the centres of four differently oriented molecules. (c) Close-up of the fitted $dI/dV$ LUMO spectra. The STM feedback was opened, $V = 2$ V and $I = 1$ nA.
four different adsorption geometries of the molecules on this surface. In addition to orientations 1 and 2 introduced above, adsorption on the pentagon (denoted 3 in figure 4(a)) and on the carbon–carbon bond between a hexagon and a pentagon (4) are present. From spectroscopic measurements performed above the centre of each molecule (figure 4(b)) the energies of the HOMO, LUMO and LUMO + 1 are determined. These energies along with similar data for other noble surfaces [4] are summarized in table 1.

The basic results which can be inferred from table 1 are, firstly, the positions of the unoccupied molecular orbitals are located closer to the Fermi level for surfaces with higher chemical reactivity. Secondly, for C_{60} adsorbed in a compact array on Au(111), a shift of the orbitals to lower energies in comparison with the single molecule is measured. Thirdly, in contrast to Cu(100) where all molecule configurations lead to nearly identical dI/dV curves, unoccupied states measured on type 1 C_{60} on Au(111) are shifted towards the Fermi level in comparison with type 2.

For noble metals, the strength of the C_{60}-surface interactions reflects the reactivity of the surfaces. C_{60} is strongly bonded on Cu, less so on Ag, and weakest on Au surfaces. Similarly, bonding is expected to be stronger with (001) than with (111) surfaces. Therefore, the Au(111) and Cu(100) surfaces investigated constitute extreme cases for investigating the influence of surfaces on the C_{60} energy levels. The measured shifts of the unoccupied states towards the Fermi level (table 1) are consistent with this scenario. The most striking observation from table 1 is the orientation dependence of the unoccupied C_{60} orbitals, which is clearly observed on Au(111) but is almost absent on Cu(100). The case of C_{60} adsorbed on Au(111) in the \((2\sqrt{3} \times 2\sqrt{3})R30^\circ\) superstructure is particularly interesting, since both the location of C_{60} on the surface and the orientation of the molecule are known. As mentioned previously, in the \((2\sqrt{3} \times 2\sqrt{3})R30^\circ\) configuration all the C_{60} adsorption sites are identical. Earlier theoretical studies predicted that the most stable configuration for a C_{60} on the lifted Au(111) surface corresponds to the molecule adsorbed on a carbon hexagon facing a hcp substrate site. This configuration corresponds to the adsorption geometry of molecule type 1 shown in figure 1(c). It is also in this case that the stronger charge transfer is predicted [15]. All the other configurations (like type-2 molecules) are expected to result in a less-stable adsorption, and thus in a smaller charge transfer. The different amount of charge transfer appears to be the origin of the 250 mV molecular orbital shift observed between type 1 and type 2 molecules. Orbital shifts have previously been reported by Grobis et al [5] for the so-called dim and bright molecules adsorbed on Ag(100). In this case, the strong interaction between the surface and the molecules leads to a reconstruction of the substrate. The resulting molecule–substrate interface geometry is different for bright and dim C_{60} molecules and is expected to be the origin of the modifications of the molecular orbitals. Silien et al [7] have reported orbital shifts for different C_{60} adsorbed on Cu(111). Here, the orientation of the C_{60} is deduced from the STM image, but no statement about the adsorption sites are provided. Rogero et al [6] described a similar shift for C_{60} molecules in a \((7 \times 7)\) superstructure on Au(111). In this case, the position of C_{60} on the surface is well defined but the orientation of the C_{60} was not resolved. The superstructure provides two different sites for the C_{60} relative to the hosting substrate which causes a small (50 mV) shift of the LUMO. In contrast to these measurements the case of C_{60} in the \((2\sqrt{3} \times 2\sqrt{3})R30^\circ\) reconstruction is particularly interesting, since the orientation is the only parameter which varies between type-1 and type-2 molecules. Our results constitute therefore the first experiment which address specifically the influence of the orientation of C_{60} adsorbed on Au(111) on its electronic properties.
On Cu(100), the unoccupied orbitals appear to be independent of both molecular orientation and location over the substrate lattice. Since this statement is based on measurements from single locations above the molecules—detailed dI/dV maps for spatial averaging are not presently available—a small shift cannot be excluded. Nevertheless, for the strongly coupled system C₆₀ on Cu(100) the orientation of the molecules seems to have no drastic effect on the orbital energies.

Finally, we discuss the influence of intermolecular interactions on electronic properties of C₆₀. Recent studies have shown a variation of C₆₀ orbitals when inserted into a molecular host network [20]. Similarly, other molecules adsorbed on Au(111) exhibit different molecular orbital energies depending on the environment they are embedded in [21, 22]. We therefore conclude that van der Waals interactions may explain electronic differences between single molecules and molecules embedded in clusters. Further, our results show that the orientation of its nearest neighbours does not significantly affect the dI/dV spectrum of a given C₆₀.

4. Conclusion

Our experiments evidence the influence of the orientation of C₆₀ molecules adsorbed on noble metal surfaces on the C₆₀ electronic properties. This phenomenon is tentatively attributed to different charge transfer between surface and molecule for different interface geometries. When the coupling between C₆₀ and surface is increased small geometrical modifications are found to play a minor role for this charge transfer. This behaviour will have to be confirmed in the future with other surfaces or extended to other molecular systems. We also hope that this study will prompt theoretical analyses which may explain in detail the striking differences observed here between strongly and weakly coupled systems.

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