Survey of structural and electronic properties of C₆₀ on close-packed metal surfaces

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Received: 3 January 2012 / Accepted: 17 February 2012 / Published online: 7 March 2012
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Abstract The adsorption of buckminsterfullerene (C₆₀) on metal surfaces has been investigated extensively for its unique geometric and electronic properties. The two-dimensional systems formed on surfaces allow studying in detail the interplay between bonding and electronic structures. Recent studies reveal that C₆₀ adsorption induces reconstruction of even the less-reactive close-packed metal surfaces. First-principles computations enable access to this important issue by providing not only detailed atomic structure but also electronic properties of the substrate–adsorbate interaction, which can be compared with various experimental techniques to determine and understand the interface structures. This review discusses in detail the ordered phases of C₆₀ monolayers on metal surfaces and the surface reconstruction induced by C₆₀ adsorption, with an emphasis on the different types of reconstruction resulting on close-packed metal surfaces. We show that the symmetry matching between C₆₀ molecules and metal surfaces determines the local adsorption configurations, while the size matching between C₆₀ molecules and the metal surface lattice determines the supercell sizes and shapes; importantly and uniquely for C₆₀, the number of surface metal atoms within one supercell determines the different types of reconstruction that can occur. The atomic structure at the molecule–metal interface is of crucial importance for the monolayer’s electronic and transport properties: these will also be discussed for the well-defined adsorption structures, especially from the perspective of tuning the electronic structure via C₆₀–metal interface reconstruction and via relative inter-C₆₀ orientations.

Introduction

The adsorption of large molecules on surfaces is gaining increasing attention because of the multitude of possible adsorption configurations, their numerous internal degrees of freedom, and the opportunities afforded by adsorbate-induced substrate reconstruction [1–13]. Buckminsterfullerene (C₆₀) adsorbed on metal surfaces, in particular, has been extensively studied for its unique geometric and electronic properties, as well as for its potential applications as basic building block for molecular scale electronic devices [14–24]. The two-dimensional systems formed on surfaces allow studying in more detail the interplay among bonding, electronic structure, and molecular orientation [25–31]. Indeed, through careful control of the number of metal atoms bonding to C₆₀, it was demonstrated that the interface of C₆₀ with metal surfaces is of crucial importance for its performance in molecular electronics and optoelectronics [27, 28].

For C₆₀ molecules chemisorbed on metal surfaces, the molecular ordering is controlled by a delicate balance between strong molecule–substrate chemical bonding and weaker inter-C₆₀ Van der Waals interactions. The C₆₀–metal bonding for chemisorption can be ionic (e.g., on Cu(111)) or covalent (e.g., on Pt(111)) [32]. The C₆₀–metal interactions can be tuned by varying the intermolecular distances and orientations through choice of the substrate material with appropriate different lattice spacings and lattice symmetry. Metal surfaces do not behave as rigid templates for the chemisorption of C₆₀ molecules, but may reconstruct substantially to accommodate the molecules, maximizing the bonding energy and lowering the total energy of the composite molecule–substrate system. However, determining the interfacial structure details and their effects on the monolayer properties with standard

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laboratory techniques [18] is complicated for C_{60} , because the interface is buried about 7 Å below the free surface, and because the C_{60} -induced reconstruction greatly multiplies the number of plausible interfacial structures. The accurate characterization of the structural and electronic properties of C_{60} on metal surfaces has been the topic of many studies with different techniques [6, 7], including scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS), diffraction methods such as surface X-ray photoelectron diffraction (SXRD) and low-energy electron diffraction (LEED), as well as density functional theory (DFT) calculations. Under favorable conditions, STM can provide images with near-atomic resolution of the molecular ordering, height, orientation, and electronic states of C_{60} on surfaces. However, STM cannot easily detect the deeply buried adsorbate-substrate interface. The close-packed metal surfaces are very flat and therefore do not allow an easy direct determination of binding sites from STM, since the different binding sites (e.g., as shown in Fig. 1d) usually have small lateral separations, e.g., only about ~ 1.3 Å apart on Cu(111)). In addition, the C_{60} molecule is sufficiently so large that even a small coupling of lateral and vertical movement in the

instrument can easily falsify a direct site determination [33]. Diffraction techniques using SXRD or LEED can better probe the atomic layers underneath the overlayer and can reveal the three-dimensional structure of the molecule-substrate interface to some extent [18, 34]. DFT-based calculations give additional access to this important and complementary information by providing not only detailed atomic structure but also electronic properties of the substrate-adsorbate interaction, which can be compared with the various experimental observations to help us determine and understand the final structure. Indeed, it has been demonstrated that the combination of DFT with STM and/or diffraction methods is a very efficient and accurate approach to determining C_{60} monolayer properties [5, 19, 29–31, 35–37].

Recent studies reveal that C_{60} can reconstruct not only the relatively reactive “open” (110) metal surfaces but also the less-reactive close-packed fcc(111) and hcp(0001) metal surfaces [18–21, 29–31, 38–41]. In this review, we discuss in detail the ordered phases of C_{60} monolayers on close-packed metal surfaces and their frequent C_{60} -induced interface reconstruction, with an emphasis on monolayers that have one C_{60} molecule per supercell. (The monolayer

Fig. 1 Symmetries of the free C_{60} buckminsterfullerene molecule (a–c) and of the clean metal fcc(111) surface at various possible C_{60} adsorption sites (d). Dashed lines represent mirror planes. Note that the hexagonal faces of C_{60} actually only have 3-fold rotational symmetry, since their adjacent faces alternate between being hexagonal and pentagonal, while the pentagons have full five-fold symmetry. In d, full lines denote the top outermost metal layer lattice, while circles and crosses denote the second and third deeper layers, respectively. The hollow sites can be either “hcp hollows” or “fcc hollows”, depending on whether they continue the fcc or hcp bulk layer stacking sequence

is here defined as the saturation coverage of the first adsorbed layer.) We will explain how the various surface lattice spacings of different metals, such as Cu(111), Pt(111), and Ag(111), result in different supercell sizes and shapes, and cause different types of reconstruction upon C_{60} adsorption. The adsorption on other low-Miller-index surfaces will also be mentioned. Structures containing several or many inequivalent molecules per supercell (i.e., molecules in different adsorption configurations) will be discussed as well, although their interface structure is generally less well known [19, 42–45]. The well-ordered monolayer phases usually must be prepared experimentally at higher temperatures or through sufficient post-growth annealing, which could induce not only interface reconstruction, but also polymerization or even decomposition of the C_{60} molecules [36, 40, 46], and this aspect will also be discussed (note that there may be unreconstructed structures before such annealing, e.g., for C_{60} on Cu(111), even though there is no detailed structure determination for these [41]). Investigating the interfacial atomic structure is very important since the structural details determine electronic and the transport properties [26–29, 47], which will also be addressed. More discussions of the electronic properties of C_{60} monolayers, including with alkali doping, may be found in the reviews of refs. [6] and [7].

Fundamental considerations

Before discussing the adsorption of C_{60} on metal surfaces, we will in the following subsection briefly summarize the relevant properties of the free molecule and of its bulk condensed phase. Then, we can address how the monolayer C_{60} structures result from the competition between inter- C_{60} forces and C_{60} -substrate interactions. In particular, for C_{60} -substrate interactions, two aspects affect the detailed atomic structures: (1) the symmetry matching between C_{60} and substrate, which determines which part of the C_{60} molecule binds to the surface; and (2) the size matching between C_{60} and different metal lattice constants, which determines the various supercell sizes and shapes. These two aspects will be discussed in detail in two further subsections below.

Free and bulk buckminsterfullerene C_{60}

The free C_{60} molecule is highly symmetric (as shown in Fig. 1a–c), with a shape similar to a European football, consisting of 12 identical pentagons and 20 identical hexagons with carbon atoms at each corner [48]. The carbons are connected through alternating ‘double’ bonds between two adjacent hexagons and ‘single’ bonds between a hexagon and a pentagon; thus there are two different C–C

bond lengths, resp. 1.40 and 1.45 Å. The interaction between C_{60} molecules, both for solid C_{60} and for C_{60} monolayers on surfaces, is similar to the inter-layer interaction of graphite, i.e., of Van der Waals (VdW) type. Under pressure, C_{60} molecules undergo deformation, polymerization, and relative intermolecular orientation changes [49, 50]. In the bulk phase, at room temperature the C_{60} molecules adopt an fcc lattice and rotate freely so that the molecules are on average equivalent; below 260 K the C_{60} s adopt a simple cubic lattice: the four molecules in an fcc cube become orientationally ordered but in different orientations, such that the electron-rich 6:6 bonds face the electron-deficient pentagon rings of adjacent C_{60} s to minimize the electrostatic repulsion between adjacent molecules [51, 52]. C_{60} may act as either an electron acceptor or an electron donor [53]. With alkali metal doping C_{60}^{3-} becomes a superconductor, while C_{60}^{4-} becomes an insulator accompanied by drastic geometric structure changes because of the Jahn–Teller effect [54–56]. Recent studies have discovered a series of “super-atom molecular orbitals” of C_{60} for its unoccupied energy levels that lie more than 3.5 eV above the Fermi level; these orbitals are bound to the spherical potential of the cage shell rather than the central potentials of the individual carbon atoms [16, 17].

Symmetry matching

For C_{60} deposited on metal surfaces, under thermal activation, the molecules can move to find the optimum adsorption sites, and can rotate to find the best orientation: the latter involves changing the polar angle to determine what part of the cage bonds to the surface, and changing the azimuthal angle to further optimize the bonding geometry. During this process, the matching of the high symmetry sites between C_{60} and the substrate plays an important role in lowering the total energy of the C_{60} –metal composite system. Figure 1 shows the symmetries of C_{60} and those of a metal surface at different sites using fcc(111) surfaces as an example.

As seen in Fig. 1, the C_{60} molecule and the close-packed metals surfaces are highly symmetric. For C_{60} there are three main symmetries, after projection onto a surface: (1) 5-fold axes and mirror planes through the centers of two opposing pentagons (Fig. 1a); (2) 2-fold axes with pairs of mirror planes perpendicular and parallel to the edges between two hexagons (Fig. 1b); and (3) 3-fold axes and mirror planes through the centers of two opposing hexagons (Fig. 1c). For the ideal clean close-packed fcc(111) and hcp(0001) metal surfaces, there are two main kinds of symmetries (Fig. 1d): (1) if we ignore the second and deeper metal layer, there are two orthogonal mirror planes through the bridge site; (2) there are also 3-fold axes

through atop and hollow (hcp hollow and fcc hollow) sites. While Fig. 1d uses the fcc(111) surface as an example, the hcp(0001) surface has the same symmetries. For the bridge site in Fig. 1d, if we consider also the deeper layers (shown as circles and crosses), there is only one mirror plane and no 2-fold rotational axis; however, the deeper layers are expected to have little influence on site preference by C_{60} , so that the bridge site in effect has the higher symmetry of the single layer (2-fold axis and two mirror planes).

From the point of view of symmetry matching, the highest combined symmetry is obtained when a 3-fold axis of the molecule coincides with a 3-fold axis of the surface while the azimuthal orientation of the molecule makes mirror planes coincide as well: this corresponds to a hexagon of the molecule being centered and aligned with an atop or hollow site of the surface. Indeed, this *local* adsorption geometry with a 3-fold symmetry seems to be the most commonly observed, and is confirmed by DFT calculations [5, 18, 29–31, 38–41, 57–60]. For instance, with STM the molecular bonding symmetry and orientation can be determined from the symmetry seen in the images, in particular using the C_{60} lowest unoccupied molecular orbitals (LUMO), which show a three-lobed clover shape [5]. The binding configuration with 2-fold symmetry with a C–C bond oriented down toward the close-packed metal surface is less frequently observed [42, 61].

The symmetry analysis also applies to fcc(100) surfaces with a 4-fold rotation symmetry: the adsorption with 2-fold symmetry (C–C bond down) matches the substrate symmetry best and is most observed in experiments [22, 23, 25, 26, 36, 62]. Although the symmetry analysis from Fig. 1d is based on the unreconstructed surfaces, it is still valid for reconstructed surfaces if the reconstruction does not change the local symmetry, as appeared to be the case for the missing-atom reconstructions induced by C_{60} on both fcc(111) and (100) surfaces [29–31, 36]. By contrast, this symmetry analysis does not directly apply to reconstructed fcc(110) surfaces, as the C_{60} -induced rearrangement of (110) surface atoms may change their local symmetry [37, 63].

We now turn to the question of the optimum monolayer structure of C_{60} . Being nearly spherical, C_{60} tends to form hexagonal or nearly hexagonal monolayer structures on surfaces. Forming hexagonal structures on a close-packed fcc(111) or hcp(0001) surface is much easier than on fcc(100) and fcc(110) surfaces due to the difference in surface symmetries between these surfaces. On close-packed metal surfaces, C_{60} monolayers can form hexagonal structures with one molecule per supercell, while keeping the intermolecular distance close to that in its bulk C_{60} phase (about 10 Å); but on (100) and (110) surfaces the adsorption structures can be very complicated because of the symmetry mismatch of the surface (4- or 2-fold) and of the C_{60} monolayer (which prefers 3-fold): as a result, the

structures may be highly inhomogeneous and aperiodic, with C_{60} in a non-hexagonal arrangement, and each supercell containing several molecules in different, often inequivalent adsorption configurations [35–37, 63, 64]. In the following discussions of the size matching between C_{60} and metal surfaces, we focus on C_{60} on the close-packed metal surfaces, which is relatively simple, while there are many more possibilities for C_{60} on (100) and (110) surfaces.

Size matching

The average C_{60} cage diameter is about 7.0 Å (measured between nuclei), while the shortest intermolecular center-to-center distance is about 10.0 Å for C_{60} in the bulk phase. The intermolecular gap between neighboring C_{60} s is thus about 3.0 Å, which is smaller than the graphite interlayer spacing of 3.35 Å. For the (clean, unreconstructed) close-packed metal surfaces, the experimental surface lattice constant varies: for the metals which we will focus on, it is 2.56 Å for Cu(111), 2.77 Å for Pt(111), and 2.89 Å for Ag(111). The size of one C_{60} molecule (about 10 Å) closely matches four times the Cu(111) surface lattice constant (10.2 Å), or about 3.6 ($\sim\sqrt{13}$) times the Pt(111) surface lattice constant (10.0 Å), or about 3.5 ($\sim 2\sqrt{3}$) times the Ag(111) surface lattice constant (10.0 Å); the factors 4, $\sqrt{13}$, and $2\sqrt{3}$ are relative supercell lattice constants observed experimentally on Cu, Pt, and Ag, resp. (as shown in Fig. 2). We thus fully expect different cell sizes (and hence also different cell shapes) on different metal surfaces for the adsorbed C_{60} monolayers. For example, on Cu(111), a (4×4) supercell can be formed (Fig. 2a), on Pt(111), a $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ supercell can be formed (Fig. 2b), and on Ag(111), a $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ supercell can be formed (Fig. 2c). These supercell geometries deduced from the simple size matching are consistent with the observed supercells in experiments for the ordered phases of C_{60} monolayers on close-packed metal surfaces [18, 29–31]. This analysis should also apply for the hcp(0001) surfaces.

Since the inter- C_{60} VdW interaction is relatively weak compared with the C_{60} –metal chemical bonding, the inter- C_{60} separations can be changed to some extent on metal surfaces: usually one observes C_{60} monolayers with a molecular center-to-center distance in the range of about 9.5–11 Å [22, 29–32, 65]. As an example of a slightly “compressed” C_{60} monolayer, on Pt(111), in addition to the $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ phase, the denser $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ phase can also be formed, with an inter- C_{60} separation of 9.6 Å, reduced by a factor $\sqrt{(12/13)} = 0.96$. The reason why two phases can be formed on Pt(111) will be discussed in the “Further structural aspects” section.

Fig. 2 Sketch of different supercells of ordered C_{60} monolayers on fcc(111) metal surfaces. Blue solid lines denote the ideal top metal layer lattice, while circles and crosses denote the deeper layers (Color figure online)

Interface reconstruction

For the adsorption of molecules on metal surfaces, self-organization of the intact adsorbed molecules is a common process, while surface reconstruction is relatively rare; by reconstruction we mean metal–metal bond-breaking and/or bond-making. There is increasing evidence of reconstruction induced by C_{60} adsorption even for the closed-packed metal surfaces and even for relatively unreactive metals like Cu and Ag. In fact, it turns out that interface reconstruction of close-packed metal surfaces induced by large-molecule C_{60} adsorption is the rule rather than the exception [29–31]. Depending on the different substrate metal lattice spacings and hence the different supercell sizes as shown in Fig. 2, two types of interface reconstruction are observed: namely, formation of either a 1-atom hole or a 7-atom hole beneath each C_{60} that results from mass transport of the substrate atoms [18, 29–31], as shown in Fig. 3 for the 1-atom hole structure, and in Fig. 4 for the 7-atom hole structure. In these stable reconstructions, the C_{60} molecule expels one or seven surface atoms below it, and the molecule sits above the 1-atom hole or sinks into the 7-atom hole, maximizing the

bonding energy. The fact that there is an activation barrier associated with creating these vacancies explains why STM and LEED studies found that the adsorbed C_{60} molecules were more ordered after annealing the substrate at relatively high temperatures. To obtain a well-ordered C_{60} monolayer on different metal surfaces, different annealing or deposition temperatures are needed in a range of about 500–700 K. At higher temperatures, the surface atoms are sufficiently mobile that they can rearrange to accommodate the C_{60} molecule with vacancy structures, hence maximizing the bonding energy of the composite system.

Two types of reconstruction

Depending on the substrate lattice constant of different metal surfaces, different supercells with different numbers of metal atoms per supercell are formed to fit the size of C_{60} , as discussed above (Fig. 2). Different supercells with different numbers of metal atoms per cell lead to different types of reconstruction: namely, (1) for a supercell with a smaller number of metal atoms, e.g., on Ag(111) a $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ cell with 12 surface atoms per

Fig. 3 Two 1-atom hole adsorption structures. **a** C_{60} on Ag(111) with a $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ cell; and **b** C_{60} on Pt(111) with a $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ cell. The arrows indicate the supercell vectors. Only the outermost three layers of the substrate are shown

Fig. 4 Sketch of the 7-atom hole adsorption structure of C_{60} (blue) on Cu(111) in the (4×4) supercell (before structural relaxation), showing a complete C_{60} (blue) at upper right only; to better display the C_{60} –metal interface, only the bottom hexagon or the bottom 21 C atoms of C_{60} are shown elsewhere (also blue). A (4×4) supercell is outlined (in black, upper right), as well as a 7-Cu hole (in green, upper left), its surrounding 12-Cu atom edge (forming a hexagon, in green, bottom right), and two 6-Cu hexamers (in orange, bottom left); red and yellow atoms are the remaining atoms of the outermost metal layer; red metal atoms form the shortest metal–C bonds, while the yellow atoms also bond to C_{60} (after relaxation), although their bonding is less strong than for the red atoms (see Fig. 5 for the relaxed structure); green atoms form the unreconstructed second metal layer (Color figure online)

unreconstructed cell, the reconstruction forms a smaller 1-atom hole with C_{60} sitting on the hole (Fig. 3a); by contrast, (2) for a supercell with a larger number of metal atoms, e.g., on Cu(111) a (4×4) cell with 16 surface atoms per unreconstructed cell, the reconstruction forms a larger 7-atom hole with C_{60} sinking into the hole (Fig. 4). The 1-atom hole reconstruction is also formed for C_{60} on Pt(111) for the $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ cell with 13 metal atoms per cell (Fig. 3b). The reason why different types of reconstruction depend on the number of atoms per cell can be probed through a simple counting of the number of C_{60} –metal bonds, as will be discussed later.

Figure 3 sketches 1-atom hole structures for the Ag(111)- $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ [29] and Pt(111)- $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ [18] cases, in which C_{60} sits above the 1-missing-atom vacancy hole. In the 1-atom hole structures, the local bonding structures are similar for both supercells (and for both metals): C_{60} bonds with a hexagonal face down and with its mirror planes parallel to those of the substrate (note that for the periodic structure there is an azimuthal misalignment in the $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ case due to the 13.9° rotation of the superlattice results in the absence of the overall mirror symmetry). This local orientation of single C_{60} s relative to the substrate maximizes the numbers of C-metal bonds since there is a carbon atom pointing toward each of the metal atoms surrounding the vacancy site. C_{60} forms six C-metal bonds with the six lower-coordinated metal atoms surrounding the vacancy site, and these bonds are much stronger

than the C-metal bonds in the unreconstructed structures, where the silver atoms are surrounded by the maximum number of metal neighbors in the (111) surface. The stronger C-metal bonds in the reconstructed adsorption can compensate for the energy cost of forming holes, so that the reconstructed adsorption becomes more favored than the unreconstructed adsorption [29, 34].

The predominantly ionic bonding of C_{60} –Ag is weaker than the predominantly covalent bonding of C_{60} –Pt: this is because, compared to Ag, the d band of Pt is much closer to the Fermi level, which facilitates stronger band hybridization and more covalent bonding with C_{60} [29, 32]. Even though the C_{60} –Ag bonding is relatively weak, C_{60} can also reconstruct the Ag(111) surface, which shows that even molecules with weak individual (atom-to-atom) surface bonds can induce substantial substrate reconstruction to create favorable bonding between the adsorbate and the substrate [34, 66]. The C–metal bond lengths of C_{60} on Ag, Pt, and Cu (111) surfaces are listed in Table 1 and are compared with the sum of the covalent radius of C and those of metals.

Figure 4 sketches the 7-atom hole structure with a (4×4) cell, as it applies to Cu(111). The 7-atom hole can be obtained from the 1-atom hole by removing a ring of six more metal atoms surrounding the 1-atom hole. An ordered nanotemplate of 7-atom monolayer holes is formed, in which lines of top layer Cu atoms are arranged in a kagome lattice (this lattice is best seen by focusing just on the yellow atoms in Fig. 4). In the 7-atom hole structure, C_{60} bonds with a hexagon down and with its mirror planes perpendicular to those of the substrate. C_{60} sinks into the 7-atom hole, bonding with both the atoms at the hole edges and atoms in the second metal layer. In the 7-atom hole geometry, C_{60} is located on top of a hollow site of the second layer and forms three C-metal bonds with the second layer—this bonding to the second layer is similar to the most favored bonding geometry in the unreconstructed adsorption [60]. The molecular orientation maximizes the

Table 1 Several C–metal bond lengths compared with the sum of covalent radii of C and metal atoms in the 1-atom hole (Ag, Pt) and 7-atom hole (Cu) structures, (all in Å); the bond lengths are from DFT local density approximation results

	C–metal bond lengths	Sum of covalent radii
$C_{60}/\text{Ag}(111)$	2.33	2.21
$C_{60}/\text{Pt}(111)$, $2\sqrt{3}$ cell	2.08	2.12
$C_{60}/\text{Pt}(111)$, $\sqrt{13}$ cell	2.09	
$C_{60}/\text{Cu}(111)$	2.08 ^a , 2.00 ^b	2.08

^a The bond length with the second Cu layer

^b The shortest bond length with the top Cu layer

Fig. 5 Relaxed interface structure of the 7-atom hole adsorption geometry of C_{60} on Cu(111); see Fig. 4 for comparison with the unrelaxed geometry and for explanations. Note the alternating rotation of Cu hexamers (orange) and the distorted Cu hexagon (green) (Color figure online)

number of C-metal bonds to the top surface layer: C_{60} strongly bonds to six of its nine remaining metal atoms ($9 = 16 - 7$), shown in red in Figs. 4 and 5; after relaxation, C_{60} also bonds less strongly with the three other atoms (in Fig. 5, these are the three yellow atoms with white dashed circles at corners of the “distorted hexagon”). C_{60} also bonds with the other three atoms, because of the cage expansion in the bottom part of C_{60} and the distortion in the top surface layer [30].

Figure 5 shows the 7-atom hole structure on Cu(111) after structural relaxation by DFT [30] (as confirmed by detailed LEED analysis [Ref. [30], and the article of Xu G et al., in preparation]). The top Cu layer is significantly distorted, resulting in alternating rotation of the hexamers and strong distortion of the hexagonal hole edge. For each C_{60} , the six strong C–Cu bonds (to red Cu atoms) are now complemented by three weaker C–Cu bonds (to the nearest yellow Cu atoms).

The intact C_{60} molecule causes extensive reconstruction of Cu(111), structural stability of which derives from an intricate matching of the Cu lattice spacing, the (4×4) ordering, the C_{60} orientation, and the top Cu layer distortion. For other surfaces with a similar lattice constant as for Cu, such as the Ni(111) surface, the 7-atom hole reconstruction is also expected from the STM measured apparent height profile [18]. More recently, the 7-atom hole reconstruction was also observed for *individually* adsorbed C_{60} molecules (at low coverage) on the so-called elbow site of the “herringbone reconstruction” of the Au(111) surface [39] (note that at each Au(111)’s “elbow site,” the clean reconstructed surface already has a vacancy due to a single missing Au atom [67]).

STM studies on Cu(111) have provided evidence for the 7-atom hole reconstruction model from the apparent-height difference of a sample prepared with both reconstructed and unreconstructed interface areas [30, 41]. Namely, in

the experiment, the so-called core–shell islands were prepared with a two-stage method by first depositing C_{60} at 500 K (for the “core” with a reconstructed interface) and then C_{60} at 250 K (for the “shell” with an unreconstructed interface) [30]. The STM topographic height of the core region is about 2 Å lower than that of the shell region. This large height difference suggests that the interface must have large enough vacancies to let a C_{60} “sink” by about ~ 2 Å. The number of missing Cu atoms in a (4×4) supercell can be estimated from a mass-flow analysis by in situ STM monitoring of C_{60} growth, yielding seven missing Cu atoms per cell [30].

The 7-atom hole structure is significantly distorted relative to bulk atomic positions, as shown in Fig. 5; this is different from the 1-atom hole reconstruction, in which only very small displacements of the metal atoms from their bulk positions are detected for both Ag(111) and Pt(111) [18, 29–31]. This “nanopatterning” of substrates is essential to the stability of the ordered structures of molecules and can critically influence their electronic structure, which is an important aspect in the design of molecular electronic devices. The influence of interface reconstruction on electronic structure will be discussed in a later section.

Origin of different reconstructions

To better understand how the number of remaining surface metal atoms determines the type of reconstruction induced by C_{60} , it is useful to count C-metal bonds in different supercells. For this purpose, it is convenient to focus on the 7-atom hole edge comprising 12 metal atoms forming a hexagonal ring (see dark blue hexagons in Fig. 6): that hexagonal ring is present in the (4×4) , $(\sqrt{13} \times \sqrt{13})$ R13.9° and $(2\sqrt{3} \times 2\sqrt{3})$ R30° supercells, which cells are predetermined by the metal lattice constant. The crucial difference between supercells lies in the degree to which the ring edge and its atoms are shared between neighboring holes: more sharing weakens C-metal bonds and makes the 7-atom hole less favorable. In the (4×4) cell (Fig. 6a), the hexagonal edges share six corner atoms, while the six other edge atoms (red hexagon) are not shared and are closer to the location of the C_{60} (in the middle of the hole): the latter thus form six strong unshared C-metal bonds while the former produce six weaker-shared C-metal bonds. In the $(\sqrt{13} \times \sqrt{13})$ R13.9° cell (Fig. 6b), neighboring holes share more of their edges, such that each metal edge atom bonds closely to one C_{60} in one hole (red hexagon) and simultaneously more weakly to a more distant C_{60} in an adjacent hole, weakening all C-metal bonds. Finally, in the $(2\sqrt{3} \times 2\sqrt{3})$ R30° cell (Fig. 6c), the edges of adjacent holes are completely shared, so that each of the six metal edge atoms (red hexagon) makes two short C-metal bonds

Fig. 6 Sketch of 7-atom hole structures embedded in various supercells relevant to Cu **(a)**, and hypothetically to Pt **(b, c)** and Ag **(c)**; one 7-atom hole and its six surrounding neighbors are shown. Thin light blue lines denote the ideal top metal layer lattice, while small blue circles and crosses denote the deeper metal layers; large open circles denote the seven missing surface atoms. Large solid circles denote the remaining top-layer metal atoms; dark blue hexagons denote the 7-atom hole edge comprising 12 metal atoms;

red hexagons denote the six metal atoms closest to the location of C_{60} (at the center of the 7-atom hole). Structures **(b)** and **(c)** are obtained from **(a)** by sliding the top left dark-blue hexagon to the right by one or two metal unit cells, resp., while the remaining peripheral hexagons slide similarly clockwise around the central hexagon; such sliding increases the overlap between the hexagon edges (Color figure online)

(to two molecules), thereby weakening both, while each of the six other metal edge atoms makes three longer C–metal bonds (to three molecules), further weakening these already weakened bonds.

A counter-argument in the foregoing reasoning is that with shrinking unit cell, each remaining surface metal atom loses more metal neighbors, so that the remaining metal–metal bonds become stronger with shrinking unit cell, thus favoring the 7-atom hole; however, the C–metal bonds are stronger than metal–metal bonds, which tips the balance in favor of more C–metal bonds and against more metal–metal bonds.

We further point out that the reconstruction types depend neither on the substrate electronic structure nor on the C_{60} –metal bonding types (covalent or ionic). Indeed, the substrate electronic structures and C_{60} –metal bonding types are similar for Ag and Cu, while they are different for Pt. The bonding types are mainly covalent for C_{60} on Pt, and mainly ionic for C_{60} on Ag and Cu. Both Ag and Cu have full d bands, while the d bands of Pt are not full; therefore, compared to Ag and Cu, Pt has a d band much closer to the Fermi level. As a result of the above comparison, we must conclude that the reconstruction types do not depend on the substrate electronic structure; we think this is because the interface reconstruction is thermally activated by higher annealing/depositing temperatures, which can change both the electronic and the structural properties of the substrate substantially, while the lattice spacing (supercell size) remains largely unchanged.

Further structural aspects

In the preceding two sections, we have emphasized the general character of C_{60} adsorption and metal interface reconstruction. In this section, we address several related

issues, including the two C_{60} structures that exist on Pt(111), coexisting rotational overlayer domains with 0° versus 180° orientation for both the 1- and 7-atom hole structures, more complex structures with several or many inequivalent C_{60} molecules per cell, and decomposition or polymerization of C_{60} on metals surfaces.

Two phases on Pt(111)

On Pt(111), C_{60} forms two distinct phases, labeled $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ and $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ (hereafter referred to as the $\sqrt{13}$ and $2\sqrt{3}$ phases, respectively). Note that $2\sqrt{3} = \sqrt{12}$ is just 4% smaller than $\sqrt{13}$, so the $2\sqrt{3}$ phase is slightly compressed relative to the $\sqrt{13}$ phase; in terms of unit cell areas and thus density, the compression factor is $1 - 12/13 \sim 8\%$. While both phases have the same 1-atom hole reconstruction, the two phases have different relative intermolecular orientations and distances, as shown in Fig. 7. Earlier studies suggested that, while the $\sqrt{13}$ phase was found to occur alone, the $2\sqrt{3}$ phase occurred only in coexistence with the $\sqrt{13}$ phase [38, 68]. However, a more recent study has found that it is possible to isolate the two phases through careful control of the deposition and annealing temperatures [31].

C_{60} on Pt(111) can form two phases because of a unique combination of factors, even while the local metal–molecule binding structure remains the same: the particular value of the Pt lattice constant, 3.92 Å, coupled with a rotation by $30 - 13.9 = 16.1^\circ$ of the superlattice cell from $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ to $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ and the consequent relative rotation of the C_{60} molecules. These factors result in two structures that have nearly identical binding energies per surface area in spite of different inter- C_{60} geometries [31]. Detailed structural analysis shows that the $2\sqrt{3}$ phase can exist because the shortest C–C distance

Fig. 7 **a, b** Supercells (yellow boxes, doubled in both directions for ease of viewing) and adsorption geometries of C₆₀ on Pt(111) in the $(\sqrt{13} \times \sqrt{13})$ R13.9° and $(2\sqrt{3} \times 2\sqrt{3})$ R30° phases; C/Pt atoms are colored gray/blue; to display the C₆₀/Pt interface clearly, the lower C₆₀ molecules only include their bottom part; each C₆₀ sits above a Pt

vacancy. Panels (c) and (d) show the respective inter-C₆₀ face-to-face contacts viewed parallel to the surface (labeled nearest C–C distances in Å from DFT local-density approximation results) (Color figure online)

between two C₆₀ molecules is reduced by only 0.1 Å relative to the $\sqrt{13}$ phase because of a better and denser packing (Fig. 7c, d), even though the supercell length (equal to the intermolecular center-to-center distance) is reduced by 0.39 Å (from 10.0 to 9.61 Å). For pure C₆₀, the relative intermolecular orientation does not vary at low temperatures; but the orientation can change for C₆₀ in the C₆₀/Pt combined system, because the C₆₀ molecules are fixed to orientations imposed by the Pt substrate via covalent bonding with Pt, while forming differently oriented superlattices in the $\sqrt{13}$ and $2\sqrt{3}$ phases, as seen in Fig. 7.

At higher temperatures, the denser $2\sqrt{3}$ phase will be more favored, since a higher density of holes is entropically favored at higher temperatures. This may be the reason why, at higher deposition temperature (500 K), the $2\sqrt{3}$ phase alone (without $\sqrt{13}$) can be produced [31]. It is suspected that when depositing at 500 K, the 1-atom hole reconstruction occurs immediately, and we get the denser $2\sqrt{3}$ phase only, thanks to good parallel alignment of the molecules; note that the $\sqrt{13}$ unit cell length fits the bulk C₆₀ lattice better than does the $2\sqrt{3}$ phase [31]. By contrast, after deposition at RT, the C₆₀ molecules will initially have various orientations [38], and so they cannot easily fit in the tighter $2\sqrt{3}$ unit cell (Fig. 7c, d). It has moreover been observed that annealing at 500 K cannot partially change the $\sqrt{13}$ phase to the $2\sqrt{3}$ phase, while such changes may occur at even higher temperatures [38].

Coexisting 180° rotated domains

When a C₆₀ molecule is rotated by 180° (or 60°) around an axis joining two opposing hexagons (such as around the surface normal in the adsorption structures discussed here and shown in Figs. 3, 4, 5, and 7), its other hexagons and pentagons are mutually exchanged: so it does not have 180° rotational symmetry. The 3-fold rotational adsorption sites on fcc(111) and hcp(0001) also do not possess 180° rotational symmetry (due to the stacking arrangement of the second and deeper layers). Therefore, rotating the molecules by 180° around the surface normal gives a new inequivalent adsorption structure. However, the energy difference between these orientations is very small, since the symmetry is broken only by atoms that are more distant from the interface. As a result, for both the 1-atom hole and 7-atom hole reconstructions, there are coexisting “domains” with 0° versus 180° orientation of the C₆₀ molecules around their axis perpendicular to the surface. For the 1-atom hole structure, the C₆₀ mirror planes are parallel to those of the substrate; for the 7-atom hole structure, the C₆₀ mirror planes are perpendicular to those of the substrate: in each case, there are two nonequivalent such orientations of the C₆₀ molecules, one as shown in Figs. 3 and 4, and one rotated by 180°. A 180° rotation of C₆₀ around its axis perpendicular to the surface does not change the stability of the C₆₀–metal composite structure, since the overall C₆₀–metal chemical bonding and the

inter- C_{60} VdW interactions do not significantly change with 180° rotation for both the 1- and the 7-atom hole structures. Therefore, DFT calculations predict that two domains with 180° rotation coexist with essentially equal probability. Evidence from STM images and LEED calculations confirms these two coexisting domains for both the 1-atom hole and the 7-atom hole structures [5, 29–31, 41]. In addition to the above inequivalent domains with 180° rotations, in the case of the $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ structure on Pt(111), equivalent mirrored overlayer domains with a mutual 27.8° rotation coexist, namely, rotation clockwise by 13.9° , and rotation anticlockwise by 13.9° [31, 69].

More complex structures

In addition to the ordered phases of a supercell with only one C_{60} molecule, more complicated or less-ordered structures are also observed, in which several or many inequivalent C_{60} molecules exist with different orientations within each supercell. The adsorption structures depend not only on the thermal history of the sample but they are also sensitive to the initial deposition coverage [33, 70–72]. For example, on Cu(100), STM reveals that for an initial coverage of 0.5 monolayer, C_{60} orders in a one-bright-and-one-dim row sequence along the [110] direction, whereas for a coverage close to one monolayer, C_{60} orders in a two-bright-and-one-dim sequence [71].

For C_{60} on Al(111), STM studies have shown that one molecule out of three protrudes from the surface upon reconstruction, and DFT calculations suggested an irreversible (6×6) reconstruction of the system from the $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ phase [19, 20]. In the (6×6) structure, it is proposed that two of the three C_{60} s in the supercell induce the 1-atom hole reconstruction, while the two removed Al atoms form an ad-dimer in the interstice below two C_{60} s and the third C_{60} adsorbs without causing a reconstruction. The (6×6) reconstruction explains the different heights observed in STM studies, while avoiding compression of the C_{60} overlayer (note that in the Al(111)- $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ - C_{60} phase, there is a 1.1% compression in the intermolecular spacing).

For $C_{60}/Ag(100)$, the C_{60} monolayer is highly inhomogeneous and aperiodic; combined STM and DFT studies reveal that the bright–dim contrast has a definite geometric origin and that there are two types of dim C_{60} molecules, one a monomer and the other a dimer, i.e., polymerization of C_{60} s occurs [36]. For C_{60} on Ag(111) and Au(111), in addition to the adsorption with a hexagon down, co-adsorption with a C–C 6:6 bond down is reported [42, 73]. For $C_{60}/Au(111)$, in addition to the 7-atom hole at the “elbow sites” [39] and the mix of molecules with either hexagon down (with 1-atom hole reconstruction) or C–C

6:6 bond down [42], many more complicated structures are reported [43–45], all based on qualitative STM experiments: for example, a (7×7) supercell with four C_{60} s, and a $(\sqrt{589} \times \sqrt{589})R14.5^\circ$ supercell containing 49 molecules which adopt 11 different orientations, while the monolayer structure can be divided into a faulted half and an unfaulted half similar to the (7×7) reconstruction of Si(111) [43].

According to Maxwell et al. [32], the C_{60} –substrate interaction can be divided into three categories: strong predominantly covalent, intermediate predominantly ionic or covalent, and weak predominantly Van der Waals. Under thermal activation, in the case of strong C_{60} –metal interaction, such as on Ru(0001), Pt(111), and a nickel thin film, C_{60} decomposes and graphene is formed [40, 46, 74]; with intermediate C_{60} –metal interaction, such as on Cu(111) and Ag(100), C_{60} undergoes polymerization instead of decomposition [36, 46]. We thus expect that the strength of the C_{60} –substrate interaction determines the final fate of the adsorbed C_{60} under thermal activation (i.e., annealing to higher temperatures): for weak interaction, C_{60} may desorb; for intermediate interaction, C_{60} may polymerize thanks to sufficient C_{60} mobility on the surface; for strong interaction, C_{60} may decompose since strong interaction reduces the mobility of C_{60} and can break the C–C covalent bonds [40].

Electronic properties

The local atomic arrangements at the C_{60} –metal contact affect not only the stability of the structure and the strength of the bonding but also the electronic structure and transport properties of the supported molecule. Many factors affect the electronic structures of the supported C_{60} : interface reconstruction, fixed inter- C_{60} orientations due to bonding with surface atoms, co-adsorption with alkali and magnetic atoms, C_{60} polymerization, layer dependence in multilayer adsorption, etc. [29–31, 46, 55, 75, 76]. For example, by co-adsorption with alkali and magnetic atoms, the composite overlayer can be transformed from semiconducting into metallic, insulating, superconducting, and magnetic phases depending on the concentration and the nature of the dopant atoms [55, 76]. In the following, the effects of two factors on the electronic properties will be discussed in detail, namely, those of the structure of the metal– C_{60} interface and those of the inter- C_{60} interactions modified by surface bonding, since these two factors are most closely related to the structural properties discussed above. Details of the effect of interface contact on the transport properties will also be described in the following subsection.

Effects of the structure of the metal–C₆₀ interface

C₆₀ adsorbed on metal surfaces normally involves metal-to-C₆₀ electron transfer which partially occupies the C₆₀ LUMOs. For C₆₀/Cu(111), the charge transfer has been measured to range from about 1–3 electrons per C₆₀ by photoemission spectroscopy [77], while DFT calculations based on an unreconstructed interface model give a much smaller amount of charge transfer, ~ 0.8 electrons [60]. From the previous discussions, we already know that the C₆₀/Cu(111) interface structure can be either reconstructed or not depending on the thermal history of the sample. These different interface structures are of crucial importance to solve the above puzzle of various electron transfers. It emerges that the electron transfer amount does not simply depend on the substrate work function, but can depend strongly on the interface structures as well [30, 60].

Figure 8 shows the STS and PDOS curves for both the unreconstructed and reconstructed structures of C₆₀/Cu(111). Based on the interface model shown in Fig. 5, the calculated projected density of states (PDOS) compares qualitatively with the STS data. For the reconstructed structure, the LUMO-derived band energy is lowered by about 0.4 eV compared to that of the unreconstructed structure, which moves much closer to the Fermi level. Therefore, C₆₀ adsorbed on reconstructed Cu(111) can receive a much larger amount of electrons than if adsorbed on the unreconstructed Cu(111). The observed various electron transfers are then explained through a definitive interface effect that affects the electronic properties of the molecule–electrode contact.

The C₆₀–metal interface structure also affects the transport properties of the adsorbed C₆₀. For example, through careful control of the number of metal atoms (1–5 atoms) bonding to C₆₀, it was demonstrated that the conductance increases with the number of bonding atoms [27]. Thus, the concepts of “good” and “bad” contacts, commonly used in macro- and mesoscopic physics, can also be applied at the atomic scale. Furthermore, theoretical calculations show that the unreconstructed adsorption of C₆₀

(coupling less strongly to the substrate) favors the appearance of a negative differential resistance compared with the reconstructed adsorption [47]. At low coverages, due to the lack of intermolecular interactions, a larger number of local C₆₀–metal contact configurations is observed than at monolayer coverage [33, 62, 72]: a low-temperature STM study of C₆₀ on Cu(111) and K/Cu(111) at low coverages showed that the spatial distribution and the STS spectral width of the LUMO-derived states are particularly sensitive to the adsorbate–substrate contact [72]; and the spatial mapping of the spectral density of single C₆₀ molecules on Ag(100) demonstrated the need for explicitly including the substrate interaction and the STM tip trajectory to understand the observed C₆₀ local electronic structures [62].

Effect of inter-C₆₀ interactions

For C₆₀ on Pt(111), Fig. 7 shows that two phases with the same local adsorption structure exist, while the inter-C₆₀ orientations and distances of neighboring molecules differ between these two phases. DFT calculations predict that these two structures exhibit very different electronic properties because of the inter-C₆₀ interactions, as shown in Fig. 9 [31]. The dependence of the band structure for C₆₀ on relative orientation of neighboring molecules has also been reported, which is based on comparison of C₆₀ on the Ag(111) and Ag(100) surfaces [26]: since these two systems have quite different C₆₀–metal interfaces, the origin of the band structure differences is not as clear-cut as for the two structures on Pt(111).

Figure 9a–d shows the PDOS for the two phases both without (Fig. 9a, b) and with (Fig. 9c, d) Pt substrate, which help us understand the effects of C₆₀–C₆₀ and Pt–C₆₀ interactions. Figure 9a and b for the PDOS between the two phases without Pt illustrate that the differences between the inter-C₆₀ interactions of the two phases are reflected in differences in the peak shapes, including different peak broadening and splitting. These differences are due to the different inter-C₆₀ orientations and distances,

Fig. 8 **a** STS spectra and **b** calculated C₆₀ PDOS of the unreconstructed and reconstructed structure of C₆₀/Cu(111), which show a dramatic shift of the C₆₀ LUMO in the reconstructed versus the unreconstructed structure. **a** is adapted from Ref. [30]

Fig. 9 Electronic structures calculated for the two phases of $C_{60}/Pt(111)$ shown in Fig. 7. **a–d** PDOS of C_{60} in the $\sqrt{13}$ and $2\sqrt{3}$ phases, in **(a)** and **(b)** without and in **(c)** and **(d)** with Pt substrate [red lines are the PDOS (divided by 5) of the complete C_{60} ; green lines are the PDOS of the bottom six carbons that bind with Pt; blue lines are the PDOS (divided by 2) of the middle eighteen carbons near the C_{60} “equator,” bordering neighboring molecules; and $p_{x,y}$ are p orbitals along the surface parallel directions]. A smaller ordinate range is used in the PDOS plots for C_{60} with Pt to compensate for the smaller peak height with Pt because of the larger peak broadening. Also shown are the band structures of C_{60} LUMOs in the $\sqrt{13}$ **(e)** and $2\sqrt{3}$ **(f)** phases without Pt substrate (Color figure online)

especially for the PDOS near the C_{60} “equator” (blue lines in the plots). Comparison of Fig. 9a with c [and Fig. 9b with d] for the PDOS without and with Pt shows that the PDOS is also considerably affected by the Pt– C_{60} interactions: the peaks are broadened and split (or partially merged in the case of the unoccupied states in the $2\sqrt{3}$ phase). The peak positions also shift slightly. Thus, the inter- C_{60} interactions change the peak shape, including broadening and splitting; these changes are enhanced by Pt– C_{60} interactions. The different splitting of different molecular orbitals can be attributed to the different couplings for different orbitals: namely, the interactions are different for different orbitals [78]. The strength of the C_{60} –Pt interactions is shown most clearly through the broadening of the bottom carbon PDOS (green lines).

The covalent interactions result mainly in orbital hybridization, but no significant energy shift and hence very small charge transfer: The charge transfer is small and similar for both phases, as ~ 0.25 electrons are transferred from the Pt surface to each C_{60} ; this contrasts with a charge transfer of about three electrons in the $C_{60}/Cu(111)$ 7-atom hole reconstructed system. The strong covalent Pt– C_{60} interactions turn the C_{60} monolayer into a metal (states appear just below the Fermi level), which is another difference compared with the charge transfer-induced metallization of $C_{60}/Cu(111)$. Also, the simulated PDOS features using the reconstructed model better fit the experimental spectroscopic data (ultraviolet photoemission spectroscopy and metastable atom electron spectroscopy data in Ref. [79]) than with the unreconstructed model adopted in that study.

For the LUMOs of C_{60} , the effects of the Pt- C_{60} interactions on the PDOS are relatively smaller than for other orbitals shown in the PDOS plots. Therefore, it is useful to compare the band structures of the C_{60} LUMOs to evaluate the effects of inter- C_{60} interactions. The band structures of the C_{60} LUMOs would be the closest to the Fermi level on metal surfaces subject to co-adsorption doping. The LUMOs consist mainly of p orbitals pointing radially at each carbon atom, and hence, are sensitive to the C_{60} orientation [80]. Figure 9e and f show the band structures of the C_{60} LUMOs in the two phases. The band dispersions and band widths are very different for the two phases. Two key features are observed: (1) the band width is smaller for the $\sqrt{13}$ phase than for the $2\sqrt{3}$ phase; (2) the dispersion in the Γ -M direction is “out of phase”: this means that for the $2\sqrt{3}$ structure the lower two bands disperse upward and the upper band disperses downward from Γ , while for the $\sqrt{13}$ structure the lower two bands disperse downward and the upper band disperses upward from Γ . Feature 1 can be explained by the different C_{60} - C_{60} distances in the two structures: smaller distances result in stronger inter- C_{60} interactions and hence larger band width, and vice versa. Feature 2 is due to the different relative inter- C_{60} orientations between the two phases, which causes the intermolecular interaction to become “out of phase” between the bands that exhibit upward versus downward dispersions (this is illustrated in the wave function plots in Fig. 10): for the upward dispersion, the nearest interacting C atoms on neighboring molecules exhibit LUMO wave functions with the same phase; while for the downward dispersion, the LUMO wave functions have opposite phases [31]. These

results demonstrate the structural tuning of electronic properties for molecular films/junctions composed of the same materials.

Outlook

The determination of structural and electronic properties of the interface between large molecules and metal surfaces include at least the following three important issues: (1) finding the geometrical arrangement and bonding of each atom at the interface for samples prepared under various experimental conditions; (2) accounting properly for the Van der Waals interactions between the molecules and the substrate metals; and (3) developing a quantitatively reliable description of the energy level alignment between the molecule and the substrate. Regarding the first issue: The interface structures depend on the thermal history and the kinetic progress of the sample, which should correspond to different local minima of total energy calculations. However, different local minima may have similar total energies. For example, for $C_{60}/\text{Al}(111)$, a vacancy-adatoms model is proposed, while for $C_{60}/\text{Ag}(111)$ and $C_{60}/\text{Pt}(111)$, the proposed models assume that the missing atoms have moved far away (e.g., to step edges). However, vacancy structures with the expelled metal bonding as an adatom with both C_{60} and the reconstructed surface cannot be ruled out, for both structures on $\text{Ag}(111)$ and on $\text{Pt}(111)$; the difficulty exists for both total energy and diffraction methods (because the adatom's effect on the diffraction spectra is very small [29]). Regarding the second issue:

Fig. 10 C_{60} LUMO wave function plots at several special K points (indicated by arrows), for C_{60} in the $2\sqrt{3}$ (left) and $\sqrt{13}$ (right) phases; the lines across C_{60} s denote nearest inter- C_{60} directions

Van der Waals density functionals with different exchange–correlation functionals can separately treat either molecules or substrate metals quite well. However, they do not perform well for the composite molecule–metal system. Recent studies demonstrate that with an appropriately chosen exchange–correlation functional, it is possible to solve this problem [81]. Regarding the third issue: The methods need to be improved that allow correcting for the underestimation of the DFT band gap while still being applicable to the large systems which are of practical relevance [82].

Acknowledgements This study was supported in part by the City University of Hong Kong Grant 9610059; the High Performance Cluster Computing Centre, Hong Kong Baptist University, which receives funding from the Research Grants Council, University Grants Committee of the HKSAR and Hong Kong Baptist University; and the CityU Centre for Applied Computing and Interactive Media.

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