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Resonant core spectroscopies of the charge transfer interactions between C_{60} and the surfaces of Au(111), Ag(111), Cu(111) and Pt(111)

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Abstract

Charge transfer interactions between C_{60} and the metal surfaces of Ag(111), Cu(111), Au(111) and Pt(111) have been studied using synchrotron-based photoemission, resonant photoemission and X-ray absorption spectroscopies. By placing the X-ray absorption and valence band spectra on a common binding energy scale, the energetic overlap of the unoccupied molecular orbitals with the density of states of the underlying metal surface have been assessed in the context of possible charge transfer pathways. Resonant photoemission and resonant Auger data, measuring the valence region as a function of photon energy for C_{60} adsorbed on Au(111) reveals three constant high kinetic energy features associated with Auger-like core-hole decay involving an electron transferred from the surface to the LUMO of the molecule and electrons from the three highest occupied molecular orbitals, respectively and in the presence of ultra-fast charge transfer of the originally photoexcited molecule to the surface. Data for the C_{60}/Ag(111) surface reveals an additional Auger-like feature arising from a core-hole decay process involving more than one electron transferred from the surface into the LUMO. An analysis of the relative abundance of these core-hole decay channels estimates that on average 2.4 ± 0.3 electrons are transferred from the Ag(111) surface into the LUMO. A core-hole clock analysis has also been

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applied to assess the charge transfer coupling in the other direction, from the molecule to the Au(111) and Ag(111) surfaces. Resonant photoemission and resonant Auger data for C_{60} molecules adsorbed on the Pt(111) and Cu(111) surfaces are shown to exhibit no super-Auger features, which is attributed to the strong modification of the unoccupied molecular orbitals arising from stronger chemical coupling of the molecule to the surface.

Keywords: fullerenes, metal surfaces, charge transfer, resonant photoemission, core-hole clock, autoionization

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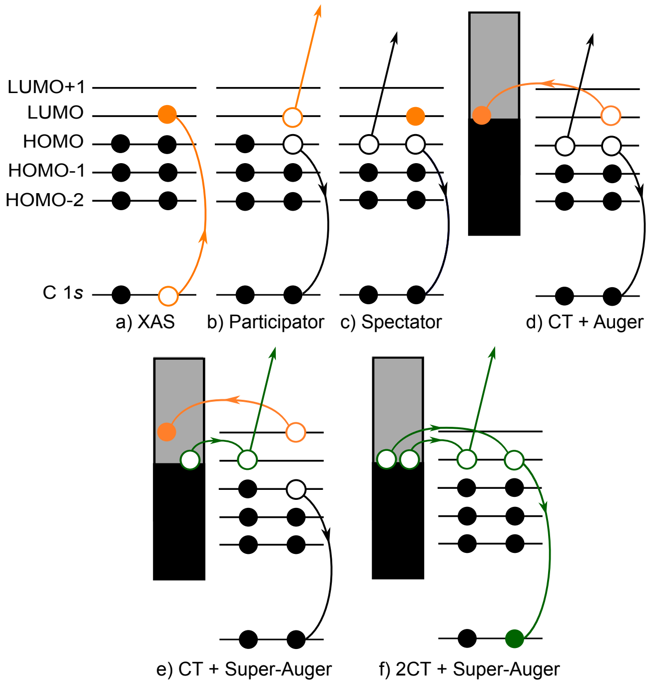
1. Introduction

Molecule-molecule and molecule-surface charge transfer interactions lie at the heart of many molecular electronics applications, in particular organic solar cells where the molecular components act as both electron donors and acceptors. Fullerenes are excellent electron acceptors for molecular electronics in general and molecular photovoltaic devices in particular.[1] Over the past two decades the majority of organic photovoltaics have focused on an approach using conjugated, semiconducting polymer electron donors (such as P3HT) with fullerene-based acceptors (such as PCBM).[2, 3]

In our previous studies of organic molecules on metal surfaces using resonant photoemission and resonant Auger spectroscopies, the transfer of electrons from a Au(111) surface into the lowest unoccupied molecular orbital (LUMO) of the molecule was shown to give rise to a new core-hole decay channel directly involving the transferred electron.[4, 5] The resulting core-hole decay process was suggested as one in which the photoexcited core-electron is localised in an unoccupied molecular orbital on the timescale of the core-hole lifetime and spectates as the electron transferred from the surface into the LUMO fills the core-hole with the energy being liberated by the emission of an electron from the highest occupied molecular orbital (HOMO). The kinetic energy of an electron emitted in such a Core/LUMO/HOMO spectator decay process is greater than that of a normal Core/HOMO/HOMO spectator decay by an amount equal to the



a) XAS b) Participator c) Spectator d) CT + Auger

e) CT + Super-Auger f) 2CT + Super-Auger

Figure 1: Schematic illustration of the key electron excitation and subsequent core-hole decay processes observed for a molecule adsorbed on a metallic surface and relevant charge transfer interactions. (a) XAS excitation of a core-level electron (orange) into an unoccupied molecular orbital, in this case the LUMO; (b) participator decay; (c) spectator decay; and (d) charge transfer of the photoexcited electron to the substrate conduction band followed by Auger decay (black and grey shaded areas represent occupied and unoccupied states of the surface respectively), (e) charge transfer of an electron (green) from the substrate valence band into the LUMO of the molecule, followed by ultra-fast charge transfer of the originally photoexcited electron into the substrate conduction band and subsequent super-Auger decay involving the electron (green) transferred from the surface, and (f) charge transfer of two electrons (green) from the substrate valence band into the LUMO of the molecule, followed by super-Auger decay involving the electrons (green) transferred from the surface (ultra-fast charge transfer of the originally excited electron assumed to take place but omitted for clarity).

HOMO-LUMO gap of the molecule, and thus referred to as *superspectator* decay. The presence of these high and constant kinetic energy features in resonant photoemission spectroscopy (RPES) can therefore provide direct evidence for charge transfer into the LUMO of the molecule. This was first observed in the case of bi-isonicotinic acid (4,4'-dicarboxy-2,2'-bipyridine) molecules adsorbed on a Au(111) surface,[4] and later for a C_{60} monolayer on Au(111).[5] In both cases, the high kinetic energy Auger-like features are not observed for molecules isolated from the surface of the substrate in a multilayer, or for the clean surface itself confirming that the core-hole decay process arises directly from the molecule-surface interaction. Similar high kinetic energy features have also been observed in a recent RPES study of bipyridine monolayers adsorbed on Au(111), epitaxial graphene on Ni(111) and graphene nanoribbons, attributed to ultrafast bidirectional charge transfer between the molecules and the surface.[6] Also of relevance here is an early RPES study of molecular nitrogen adsorbed on a graphite surface, charge transfer from the substrate to the LUMO of the core-excited molecule was observed on the timescale of the core-hole lifetime.[7]

The mechanisms for the different non-radiative core-hole decay channels available to a molecule coupled to a metal surface are schematically illustrated in Fig. 1. X-ray absorption (XAS) causes excitation of a core-level electron (orange) - in this case the C 1*s* orbital - to an unoccupied molecular orbital (Fig. 1a) after which the resulting core-hole must be filled by a higher-lying electron. In the case of *participator* decay (Fig. 1b) the originally excited electron is a direct participant in the decay process and the system is left in a final state identical to direct photoemission of the valence state involved. Participator decay therefore results in a resonant enhancement of the photoemission (RPES) and will have a constant binding energy as the photon energy increases. In the case of *spectator* decay (Fig. 1c) the originally excited electron is not a direct participant in the transition and the system is left in a two-hole final state via an Auger-like Core/HOMO/HOMO spectator decay process. The kinetic energy of a spectator electron is therefore constant and lower than that of a participator electron by at least the HOMO-LUMO separation. Alternatively, if the originally excited electron is not localised on the molecule on the timescale of the core-hole lifetime (through tunneling into the empty states in the underlying substrate or through excitation above the ionisation threshold) the core-hole will decay via a *normal Auger* process (Fig. 1d). Auger electrons also have a constant kinetic energy, which is lower that of the spectator process due to the presence in the latter of the additional electron in final state (the so called spectator shift). In this paper we consider the case in which an electron has been transferred from the metal surface into the LUMO of the molecule, whereupon that electron is available to participate in the core-hole decay resulting either in a *superspectator* decay if the originally excited electron is localised on the timescale of the core-hole lifetime, or *super-Auger* decay if not (Fig. 1e). In both cases the kinetic energies of the emitted electrons are increased by the fact that one of the participating electrons originates from the LUMO rather than the HOMO, resulting in an energetic uplift corresponding to the HOMO-LUMO separation. If two electrons were to transfer into the LUMO (Fig. 1f) this would open up an additional Core/LUMO/LUMO super-Auger decay process, allowing additional energy to be transferred to the emitted electron since now both electrons involved in the transition originate from the LUMO. By considering the energies of the electrons measured in RPES as a function of photon energy over the C 1s absorption edge in this study we interpret the data in terms of these available core-hole decay processes and infer from these the charge transfer processes and dynamics at the C_{60}/metal surface. As superspectator and super-Auger processes rely on the transfer of electrons from the surface into the LUMO of the molecule, by tuning the coupling strength of the molecule, in this case C_{60} with the metal surface it is in principle possible to observe differences in the intensity of these channels in the RPES. Previous studies have found varying amounts of charge transfer between different metal surfaces and adsorbed C_{60} molecules,[8, 9, 10, 11, 12, 13, 14, 15] and in this paper we explore the effect that changes in the adsorption interaction have on the presence of high constant kinetic energy core-hole decay features for C_{60} molecules adsorbed at Au(111), Ag(111), Cu(111) and Pt(111) surfaces.

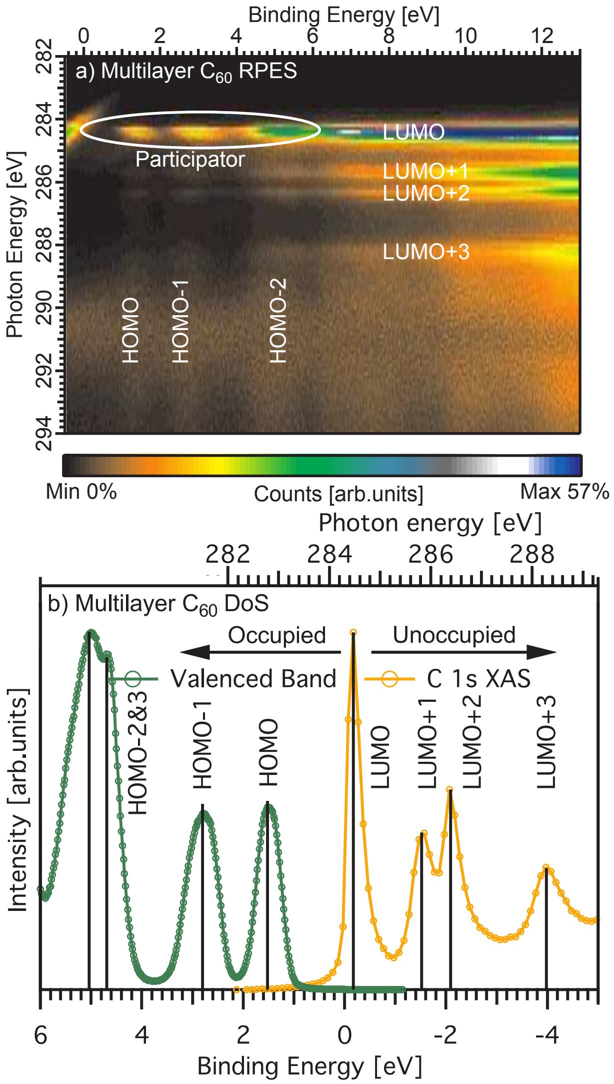


Figure 2: a) RPES for a C_{60} multilayer obtained by measuring the valence photoemission whilst incrementally increasing the photon energy over the C 1s absorption edge, and b) a density of states plot for multilayer of C_{60} obtained by placing the C 1s XAS on a common binding energy scale with the valence band photoemission (hν = 60 eV).

2. Experiment

Experiments were carried out at the I311 beamline on the MAX-II storage ring at the MAX-lab facility in Lund, Sweden. The beamline covered a photon energy range of 30-1500 eV with a resolution of 4 meV-1.4 eV respectively. The spot size was 0.5 mm horizontally and 0.1 mm vertically. The end-station was equipped with a *Scienta* SES200 hemispherical electron analyser. The radiation had a high degree of elliptical polarisation, and is considered as linearly polarised, further details of I311 can be found elsewhere.[16] The base pressure in the analysis chamber was in the low 10^{-10}mbar range and in the preparation chamber the mid 10^{-10}mbar region. The metal substrates were all circular single crystals mounted to loops of tungsten wire to provide resistive heating. Thermocouples were mounted directly to each crystal.

The Cu(111) single crystal was cleaned with 2 kV Ar^+ ion sputtering for 20 min, followed by annealing at 470 °C for 20 min. The Au(111) and Ag(111) single crystals were cleaned in a similar manner, but with annealing temperatures of 600 °C and 550 °C, respectively. The Pt(111) single crystal was cleaned with 2 kV Ar^+ ion sputtering for 20 min, follwed by annealing in O_2 at 10^{-7}mbar for 10 min at 670 °C, followed by a flash anneal to 800 °C in ultra-high vacuum (UHV).[11] For all crystals sputtering and annealing cycles were repeated until C 1*s* and O 1*s* peaks were no longer observable by x-ray photoemission spectroscopy (XPS), and the metal core-level spectra exhibited the characteristic metallic line shapes. All XPS was measured at normal emission while RPES and XAS were measured at normal incidence in order to increase surface sensitivity and thus minimize the contribution of direct photoemission of the substrate valence band.

A multilayer of C_{60} was thermally evaporated from a Knudsen-type cell at approximately ∼360 °C for 20 min. The samples were located at a distance of approximately 20 cm and held at room temperature. Following multilayer deposition the substrate photoemission peaks were completely suppressed and the characteristic shake-up structure and symmetric main peak observed in the

C 1*s* spectrum.[17] C_{60} monolayers were prepared by heating the samples to 300 °C for 10 min to desorb the physisorbed multilayers, leaving only the more strongly bound/chemisorbed C_{60} monolayer. The presence of a monolayer was confirmed by the emergence of the characteristic asymmetry of the C 1*s* peak and modification of the shake-up features.[18, 19]

For resonant photoemission spectroscopy (RPES) and x-ray absorption spectroscopy (XAS) measurements the beamline was set such that the photon energy resolution was 50 meV for photons of 340 eV. A taper of 3 mm was applied to the undulator to reduce the intensity variation of the radiation over the photon energy range of the measurement. The analyser was set to record spectra in fixed mode with an energy resolution of 200 meV, in order to give the best compromise between signal and resolution. The photon energy scale for the RPES data was calibrated to the kinetic energy difference of the C 1*s* photoemission peak measured with first and second order x-rays. The binding energy scale of the RPES and all photoemission data was calibrated to the Fermi level of the metal. XAS and RPES data were divided through by the XAS spectra of the clean surface in order to account for variations in flux as a function of photon energy. We note that the 'carbon dip'[16] arising from surface contamination of the beamline optics meant that close to 291 eV photon energy the photon counts are effectively zero, resulting in a narrow band of lost information observed in the RPES data sets. To enhance the weaker features of interest in the RPES data the intensity scales have been clipped to the indicated range.

3. Results

3.1. C_{60} multilayer

The C 1*s* RPES data for a C_{60} multilayer is shown in Fig. 2a. When the excitation photon energy matches the LUMO resonance (284.2 eV) there is intense absorption and subsequent non-radiative core-hole decay. Three bright features can be observed in the RPES data at this photon energy, centred around binding energies of 1.5, 3 and 5 eV, which correspond to the binding energies of the

HOMO, HOMO-1 and HOMO-2,3 respectively. These features are attributed to a resonant enhancement of the photoemission of the relevant occupied molecular orbitals due to participator decay involving the originally photoexcited electron localised in the LUMO on the timescale of the core-hole lifetime. Above a binding energy of around 6 eV we observe an intense band of electrons attributed to spectator and Auger decay (see Fig. 1). As the photon energy is increased over the LUMO+1,+2 and +3 resonances the constant kinetic energy spectator and Auger features drift out of the binding energy window to higher binding energy. Although weaker than for the LUMO, participator enhancements of the HOMOs are also observed for all three of the higher lying resonances (the reduced intensity is due to matrix element effects arising from the different orbital overlaps). The diagonal line in the upper left corner is due to the C 1s core-level excited by second order x-rays from the monochromator. Fig. 2b shows the density of states for multilayer C_{60} molecules constructed by placing the valence band (occupied molecular orbitals) and C 1s XAS (unoccupied molecular orbitals) on a common binding energy scale, using procedures described elsewhere.[20]

3.2. C_{60}/Au(111) monolayer

The C 1s RPES data for a C_{60} monolayer adsorbed on the Au(111) surface is shown in Fig. 3a. At the LUMO resonance around 284 eV photon energy three enhancements are observed at the binding energies of the HOMO, HOMO-1 and HOMO-2,3 similar to the multilayer data. These features are again attributed to the same participator decay process that gives rise to these features for the multilayer. Electrons excited from the C 1s core level into the LUMO are able to participate in the core-hole decay due to being localised in that orbital on the timescale of the core-hole lifetime. Fig. 3b shows the valence band photoemission and C 1s XAS placed on a common binding energy scale to determine how the unoccupied molecular orbitals of the core-excited C_{60} monolayer overlap with the filled and empty densities of states in the Au(111) surface. The LUMO crosses the Fermi level and therefore partially overlaps with filled states in the surface into which charge transfer from those vibrational states of the LUMO

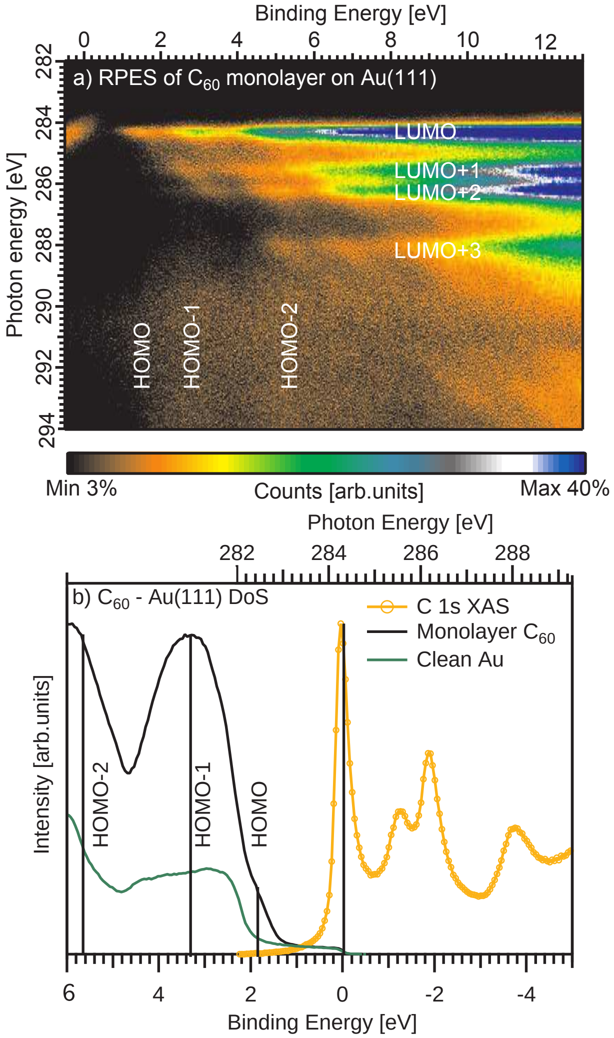


Figure 3: (a) C 1*s* RPES plot for monolayer C_{60} adsorbed on the Au(111) surface, exhibiting three diagonal constant high kinetic energy lines, (b) density of states plot for the C_{60}/Au(111) monolayer prepared in the same way as in Fig. 2b.

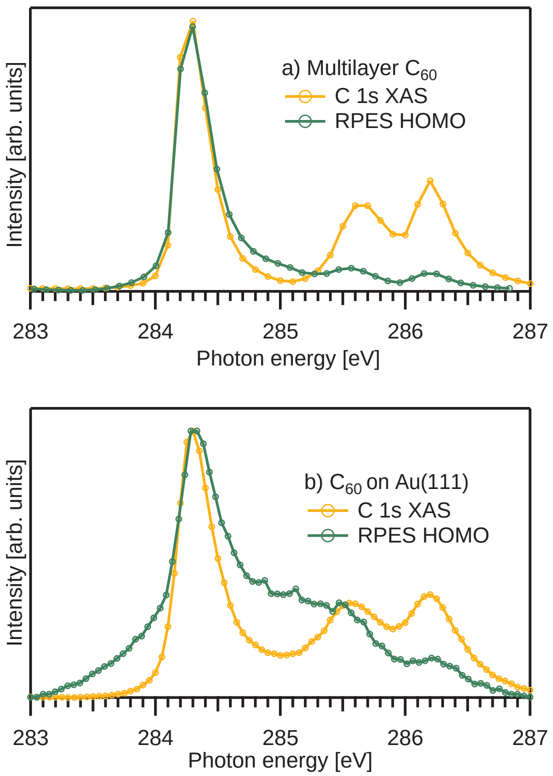


Figure 4: C 1*s* XAS and RPES traces for a) isolated molecules, and b) a monolayer of C_{60} on Au(111) obtained by integrating Auger (XAS) and participator (RPES) regions of Fig. 2a and Fig. 3a, respectively.

of the molecule will be forbidden. These localised core-excited electrons can also play the role of a spectator in the decay process resulting in an Auger-like Core/Valence/Valence spectator transition (see Fig. 1c) that together with normal Auger decay gives rise to a broad constant kinetic energy feature on the high binding energy side of the data.

Three distinct constant kinetic energy features can also be observed in the RPES data as diagonal lines that track back to the participator signals at the HOMO, HOMO-1 and HOMO-2 binding energies at the LUMO resonance. These features are attributed to an Auger-like decay process in which an electron has been transferred from the surface into the LUMO of the molecule. Since the LUMO lies just below the Fermi level (as shown in Fig. 3b), charge transfer from the surface into those vibrational states of the molecule that overlap with the filled states of the surface is possible. The three diagonal features are attributed to Auger-like core-hole decay involving Core/LUMO/HOMO (see Fig. 1d), Core/LUMO/HOMO-1, and Core/LUMO/HOMO-2 transitions made possible by a partially occupied LUMO. In the case where the originally photoexcited electron is localised on the timescale of the core-hole lifetime these will be spectator decay processes, while in the case where it tunnels into empty states in the surface on this same timescale they will be true Auger processes (Fig. 1d).

Charge transfer in the other direction - from the molecule into the unoccupied states of the surface - can be investigated by considering the participator electrons in RPES. By comparing the relative intensities of the participator channel to the XAS for both the monolayer and multilayer we can estimate the timescale of the charge transfer dynamics.[21] XAS represents the full intensity of the unoccupied levels, whereas in RPES the unoccupied states may be depleted by charge transfer from the molecule into the substrate. Charge transfer competes with the core-hole decay so to have an observable effect on the intensity of the participator channel it would need to be on the same timescale as the C 1s core-hole lifetime. The participator channels are maximally populated in the multilayer since the excited electron cannot transfer from the uncoupled molecule to the surface (nor indeed to neighbouring molecules, which for the LUMO is completely inhibited by the excitonic effect of the core hole), this represents the maximum intensity of the participator channel. Depletion of this channel in the monolayer is therefore indicative of charge transfer to the surface on the timescale of the core-hole lifetime. Line traces for the C 1s XAS and RPES are shown in Fig. 4, the traces where made by integrating over the relevant binding energy window as a function of photon energy. The RPES trace is an integration over the HOMO region ($1-3$ eV), while the XAS region is an integration over the normal Auger region (above 10 eV).

In principle, a charge transfer time for electron transfer out of a particular unoccupied molecular orbital can be calculated using equation 1,

$$\tau_{EI} = \tau_{CH} \frac{I_{RPES}^{mono}/I_{XAS}^{mono}}{I_{RPES}^{multi}/I_{XAS}^{multi} - I_{RPES}^{mono}/I_{XAS}^{mono}} \tag{1}$$

where the $I_{RPES}^{mono}/I_{XAS}^{mono}$ terms represent the relative intensities of the participator channel in the RPES as a fraction of the total x-ray absorption for the relevant molecular orbital given by the XAS. The $I_{RPES}^{multi}/I_{XAS}^{multi}$ term represents the fraction of participator electrons that would be expected in the absence of charge transfer as determined from the decoupled molecules in the multilayer film. The lifetime of the C 1s core-hole is given by τ_{CH} and is approximately 6.6 fs.[22] For a complete discussion of the core-hole clock implementation of RPES, including derivation of this equation, we direct the reader to Br$\ddot{u}$hwiler *et al.*[21] A normalisation of the monolayer and multilayer data is typically achieved by considering a molecular orbital for which charge transfer is forbidden in all situations. This is often achieved by normalisation to the LUMO intensity in cases where this orbital lies energetically well below the conduction band edge or the Fermi level of the surface to which the adsorbed molecules are coupled. However, in the case of C_{60} on Au(111) the LUMO straddles the Fermi level so that charge transfer is possible from those vibrational levels of the LUMO that overlap with the empty states above the Fermi level. A convenient normalisation point for this system and by extension a quantitative timescale for the charge transfer dynamics therefore cannot be found. Nevertheless, the data shown in Fig. 4 have been normalised to the intensity at the LUMO resonance for both the monolayer and multilayer in order to assess qualitatively the charge transfer coupling of the different molecular orbitals with the Au(111) surface.

For both the C_{60} multilayer and the monolayer on Au(111) there is a significant participator (RPES) signal for all three of the unoccupied molecular orbitals probed. This implies that the core-excited electrons are localised in the LUMO, LUMO+1 and LUMO+2 long enough to participate in the core-hole decay and is indicative of a slow rate of charge transfer to the surface even for those molecular orbitals that overlap with empty states above the Fermi level. The monolayer RPES integration in Fig. 4 contains additional intensity around 285 eV absorption energy resulting from the highest kinetic energy Auger-like feature which overlaps the integration window at the LUMO+1 photon energy. A quantitative analysis concerning the LUMO+1 is not possible, however the region around the LUMO+2 lies beyond affected energy range and thus the intensity of the LUMO+2 participator channel can be assessed relative to the LUMO. By curve fitting the spectra, $I^{mono}_{RPES}/I^{mono}_{XAS}$ and $I^{multi}_{RPES}/I^{multi}_{XAS}$ for the LUMO+2 orbital were found to be 0.35 ± 0.04 and 0.15 ± 0.01 respectively. This increase in ratio is indicative of charge transfer from the LUMO of the core-excited molecule into the unoccupied density of states in the surface on a timescale comparable to the core-hole lifetime, which is forbidden for the multilayer but becomes allowed on the Au(111) surface.

3.3. C_{60}/Ag(111) monolayer

The C 1*s* RPES data for a C_{60} monolayer adsorbed on the Ag(111) surface is shown in Fig. 5. At the LUMO resonance around 284 eV photon energy three enhancements are observed at the binding energies of the HOMO, HOMO-1 and HOMO-2,3 similar to those observed for both the multilayer film and the C_{60} monolayer adsorbed on the Au(111) surface. These features are again attributed to participator decay involving the electron localised in the LUMO

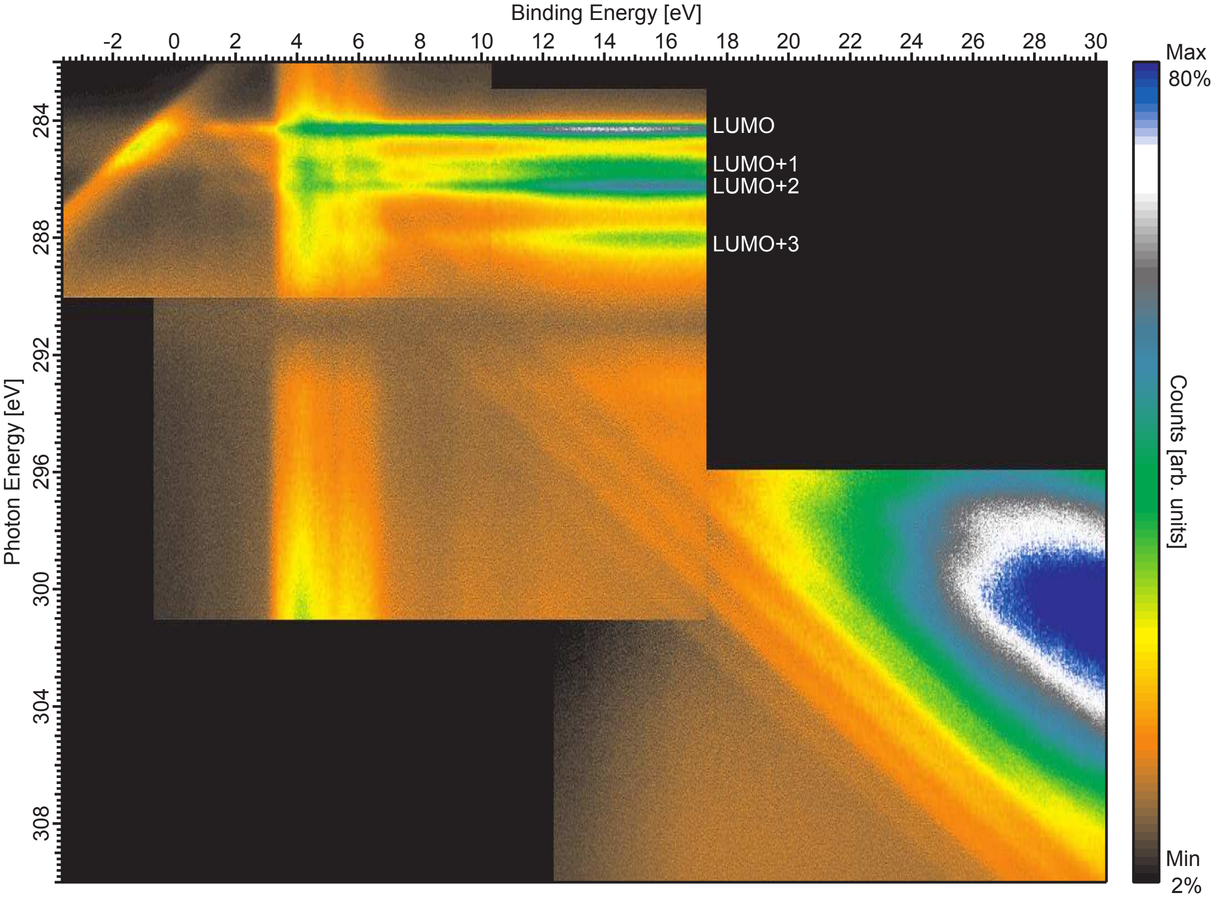


Figure 5: C 1*s* RPES plot for a C_{60} monolayer adsorbed on a Ag(111) surface, constructed from three separate datasets to show the full extent of the constant high kinetic energy Auger-like features as the photon energy is increased above the LUMO resonances and above the ionisation threshold.

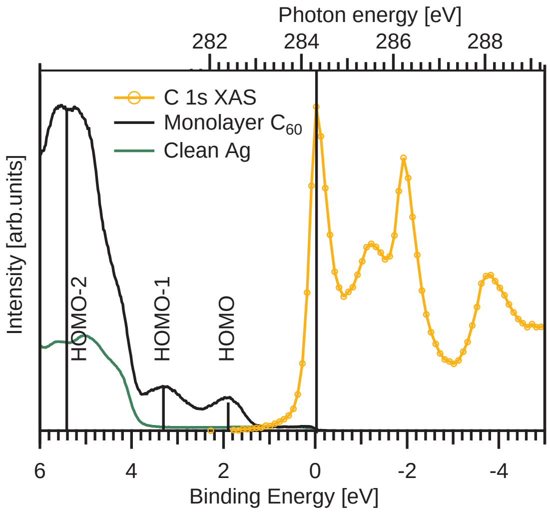


Figure 6: Density of states plot for the C_{60} monolayer adsorbed on the Ag(111) surface.

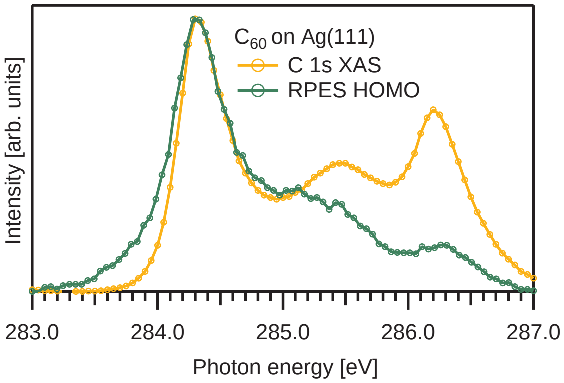


Figure 7: C 1s XAS and RPES traces for the C_{60} monolayer adsorbed on the Ag(111) surface.

on the timescale of the core-hole lifetime and electrons from each of the highest occupied molecular orbitals respectively. The vertical band of intensity between 3 and 7 eV binding energy is due to direct photoemission of the valence band of the underlying metal surface, which is more evident for Ag(111) than Au(111) due to a larger photionisation cross section for the Ag $4d$ states compared to the Au $5d$ state (0.73 and 0.19 Mbarn, respectively).[23, 24]

Three constant high kinetic energy features can be seen to track back to the binding energy positions of the HOMO, HOMO-1 and HOMO-2,3 at the LUMO resonance. These are attributed to the same Auger-like decay transitions presented for the C_{60}/Au(111) in section 3.2. In order to explore how these features develop as the absorption photon energy is increased further above resonance Fig. 5 is composed of three RPES datasets that span a binding energy window up to 30 eV and a photon energy up to 310 eV. The three features associated with the Core/LUMO/HOMO, Core/LUMO/HOMO-1 and Core/LUMO/HOMO-2 Auger-like transitions are clearly observed at higher absorption energies. Moreover, a fourth, slightly weaker and even higher kinetic energy feature is also observed. The kinetic energy of this line is approximately 2 eV higher than the aforementioned Core/LUMO/HOMO feature. This energy shift is consistent with the HOMO-LUMO separation of the C_{60} molecule as measured in the core-excited state by placing the valence band and C1s XAS on a common binding energy scale as shown in Fig. 6. Confirmation of the kinetic energy shift and an indication of the origin of this highest kinetic energy line is found by extrapolating back to the LUMO resonance, where it intersects with a binding energy consistent with the LUMO itself. Indeed, a careful inspection of the RPES data shown in Fig. 5 reveals a weak enhancement at a binding energy of 0 eV at the LUMO resonance, consistent with the position of the LUMO in Fig. 6. This enhancement is attributed to participator decay of the partially occupied LUMO at the LUMO resonance. Such a weak enhancement is only observable in this data due to the nature of the measurement that reveals the increased intensity superimposed on the second order C $1s$ peak with which it coincides. In the case where the originally excited electron is localised on the timescale of the core-hole lifetime, the highest constant kinetic energy line observed in the C_{60}/Ag(111) data is attributed to a Core/LUMO/LUMO spectator transition, which can only take place if more than one electron is transferred from the silver surface into the LUMO (see Fig. 1f).

A core hole clock analysis of the RPES data for the C_{60} monolayer on Ag(111) is shown in Fig. 7 normalised as for Au(111) to the intensity at the LUMO resonance. The ratio of participator electrons to x-ray absorption for the LUMO+2 in this case is $I^{mono}_{RPES}/I^{mono}_{XAS}$ is 0.25 ± 0.3, compared to the multilayer value of 0.15 ± 0.01. As in the case for Au(111) this increase in ratio is indicative of charge transfer from the LUMO of the core-excited molecule into the unoccupied density of states in the surface on a timescale comparable to the core-hole lifetime.

3.4. C_{60}/Cu(111) monolayer

The C 1*s* RPES data for a C_{60} monolayer adsorbed on the Cu(111) surface is shown in Fig. 8a. The data is dominated by the valence states of the copper surface due to the large photoionisation cross section of the Cu 3*d* states at these photon energies (1.2 Mbarn),[23, 24] observed as an intense vertical band from 1 eV to 5 eV binding energy. Participator enhancements of the HOMOs, if present, are too weak to observe in the RPES data for Cu(111) and no distinct narrow constant kinetic energy features are observed unlike the data for Au(111) and Ag(111). The density of states plot is shown in Fig. 8b, and a substantial modification of the unoccupied molecular orbitals compared with the multilayer is observed. There is no distinct LUMO resonance observed around 0 eV binding energy. This is consistent with substantial charge transfer into the LUMO of the molecule due to the adsorption interaction with the surface. The occupied density of states for the molecule shown also in Fig. 8b exhibits some intensity just below the Fermi level consistent with charge transfer into the LUMO, which is now observed as an occupied molecular orbital. In addition to a partially filled LUMO state, the valence spectra exhibit four occupied molecular peaks attributed to the HOMO to HOMO-3 orbitals. The binding

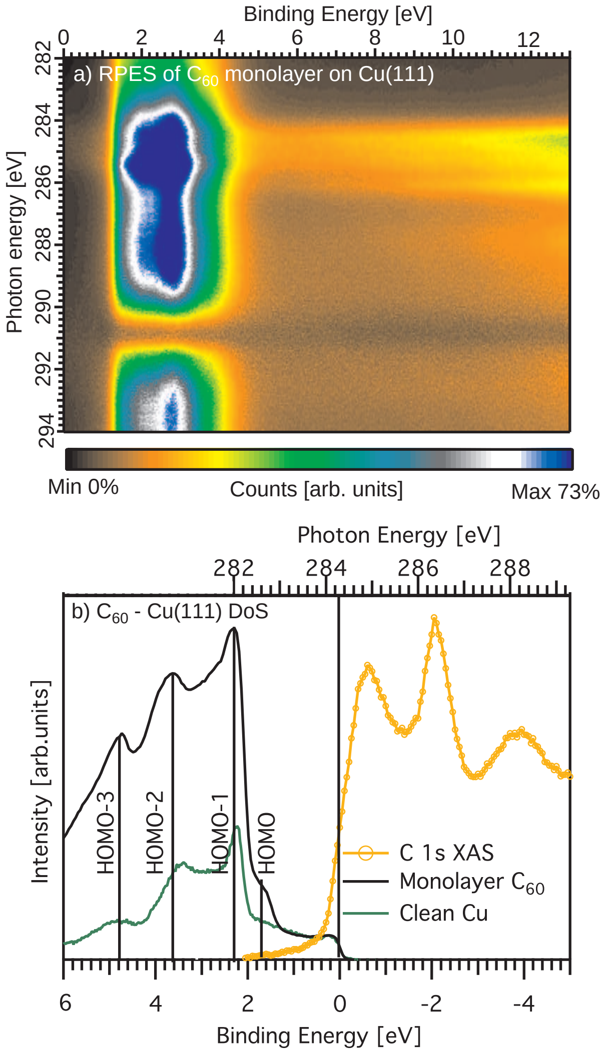


Figure 8: a) RPES and b) density of states plot for the C_{60}/Cu(111) monolayer.

energies of these orbitals are shifted relative to the multilayer, especially the HOMO-1 and HOMO-2 peaks. This is indicative of the molecules still intact on the surface but forming a relatively strong chemical interaction with the surface. The absence of any high kinetic energy Auger features for the C_{60} monolayer adsorbed on the Cu(111) surface is notable since one might expect such features to be more intense where more electron density is transferred to the molecule.

3.5. C_{60}/Pt(111) monolayer

The C 1*s* RPES data for a C_{60} monolayer adsorbed on the Pt(111) surface is shown in Fig. 9a. The data is dominated only by the Auger decay feature observed at the absorption energies of the lowest unoccupied molecular orbitals, with virtually no contribution from the underlying surface due to the low photoionisation cross section of the Pt 5*d* states at these photon energies (0.098 Mbarn).[23, 24] The density of states plot is shown in Fig. 9b revealing a substantial modification of the molecular orbitals compared with the multilayer, consistent with the much stronger chemical interaction with the surface facilitated by the Pt *d* band located much closer to the Fermi level than for gold or silver, leading to strong band hybridisation and more covalent bonding.[25] The LUMO of the chemisorbed molecule lies almost entirely above the Fermi level so charge transfer into this state from the surface in the core-excited state is not possible. Based on the data for Au(111) and Ag(111), charge transfer into the LUMO is required for the Core/LUMO/HOMO super-spectator/super-Auger decay channel to be populated, and the absence of this or similar features for the C_{60}/Pt(111) monolayer is consistent with a negligible energetic overlap of the LUMO with the occupied density of states in the surface.

4. Discussion

The resonant photoemission and resonant Auger data for monolayers of C_{60} on metal surfaces presented in this paper show evidence for a series of Auger-like core-hole decay processes in which electrons present in the LUMO at the time of

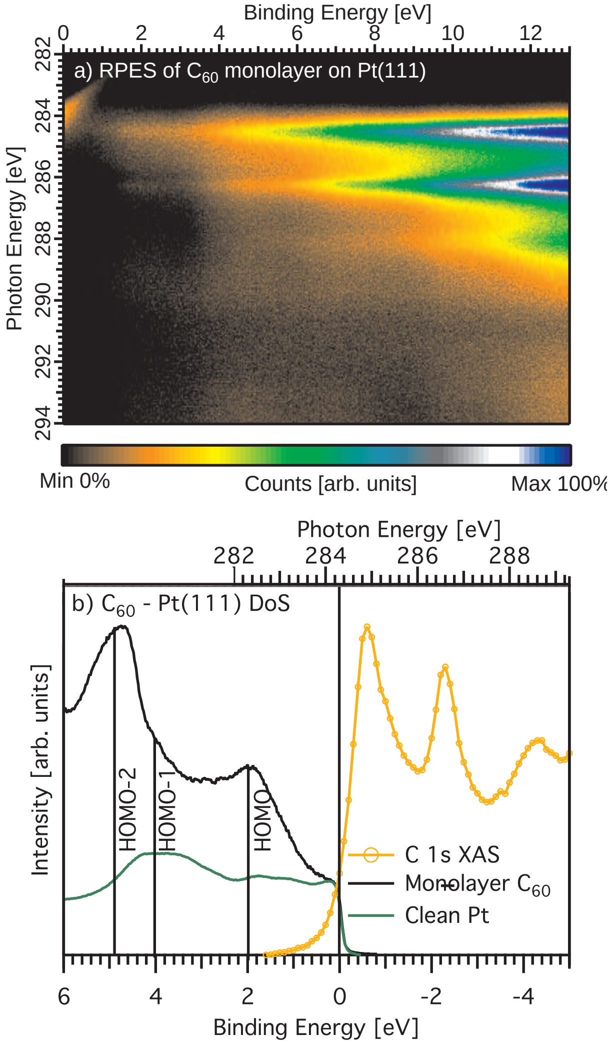


Figure 9: a) RPES and b) density of states plot for the C_{60}/Pt(111) monolayer.

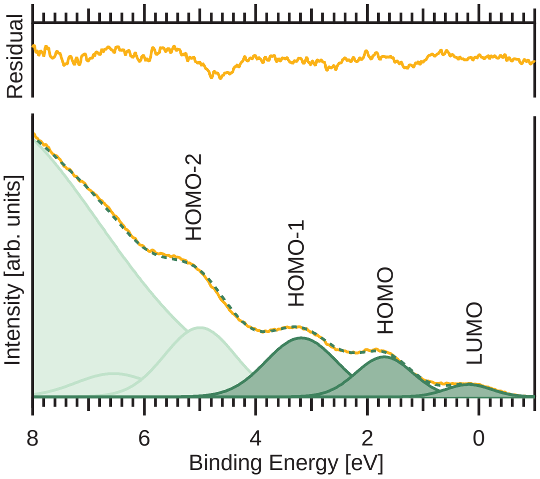


Figure 10: Integrated intensity over the super-Auger features as a function of constant kinetic energy in the photon energy region from 300 to 305 eV photon energy in Fig. 5 for the C_{60}/Ag(111) monolayer. The spectrum has been converted to a binding energy scale by extrapolating back to the binding energy positions at the LUMO resonance.

the core-hole decay play a direct role in filling the core-hole. While it is possible that these transitions could result from the originally excited electron losing coherence before the core-hole decay (due to intraband decay, delocalization or scattering) it is reasonable to consider that these features arise from the participation of electrons transferred from the metal surface into the LUMO - either through ionic bond formation or charge transfer screening.[7] Three questions remain: i) whether or not there is simultaneously ultra-fast charge transfer from the molecule to the surface on the timescale of the core-hole lifetime, ii) whether or not the charge transfer from the surface to the LUMO occurs already in the ground state or only in the core-excited state (in which case it would also be ultra-fast on the timescale of the core-hole lifetime of a few fs), and iii) whether or not it is possible to estimate how much electron density is transferred into the LUMO.

In the case of C_{60}/Au(111) three constant high kinetic energy features are observed separated by the energy spacing of the three highest occupied molecular orbitals and track back the binding energies of those orbitals at the LUMO resonance. If we consider the energy levels schematically represented in Fig. 1 and perform a *Gedankenexperiment* for core-excitation to the LUMO, we find three different scenarios of core-hole decay using only the electrons intrinsic to the molecule. Participator decay in this case (Fig. 1b) leaves the system in a final state identical to photoemission from the HOMO. Participator electrons will therefore be observed in the RPES dataset at the binding energy of the HOMO regardless of the incident photon energy. Spectator decay in the illustrated case (Fig. 1c) leaves the system in a final state similar to photoemission from the HOMO plus an excitation of an electron from the HOMO to the LUMO. These electrons have a constant kinetic energy and when excited with photons corresponding to the LUMO resonance will therefore be observed in the RPES data at a binding energy that is shifted by an amount corresponding to the HOMO-LUMO gap to higher binding energy than the HOMO, and by extension the participator. Spectator electrons, since they always involve the same energy levels (in this case Core/HOMO/HOMO) will track with constant kinetic energy. Both participator and spectator decay require the originally photoexcited electron to be localised in the core-excited molecule on the timescale of the core-hole lifetime (a few fs). If on the other hand it tunnels into the conduction band of the coupled surface the system will undergo Auger decay. Auger decay in the illustrated case (Fig. 1d) leaves the system in a state similar to spectator decay plus an excitation of an electron from the LUMO out of the molecule. Auger electrons again have a constant kinetic energy and at the LUMO resonance will appear in the RPES at a binding energy that is shifted to even higher binding energy than the spectator feature by an amount corresponding to the cost of removing the electron from the LUMO (the energy difference between the normal Auger and spectator decay is referred to as the spectator shift, which for C_{60} is on the order of 2 eV[21]). So while Auger and spectator electrons track with constant kinetic energy as a function of increasing photon energy, they cannot track back to the binding energy of the HOMO at the LUMO resonance because no transition exists using only the electrons intrinsic to the molecule that can result in such a high kinetic energy electron emission.

To understand the origin of the high kinetic energy Auger-like features observed for C_{60}/Au(111) we need to consider charge transfer from the metal surface into the LUMO of the molecule, schematically shown in the lower half of Fig. 1. A constant kinetic energy feature that tracks back to the binding energy of the HOMO at the LUMO resonance requires an Auger-like core-hole decay process that leaves the system in a final state identical to photoemission from the HOMO. The corresponding *Gedankenexperiment* is represented in Fig. 1e, where the core-hole is filled by an electron from the HOMO as in previous schemes and the emitted electron is now the electron that was transferred from the surface into the LUMO. However, this scheme also requires that the originally photoexcited electron tunnels into the substrate on the timescale of the core-hole lifetime, otherwise the kinetic energy would be increased due to the presence of that electron in the previously unoccupied molecular orbital (a spectator shift). This core-hole decay channel is therefore Auger decay involving an electron transferred to the LUMO from the surface and will appear in the RPES as a constant kinetic energy feature (since the photoexcited electron does not play a role) that tracks back to the position of the HOMO at the LUMO resonance. The lower kinetic energy features that track back to the HOMO-1 and HOMO-2/3 are explained by the analogous transitions where the electrons that fill the core-hole originate from those orbitals respectively.

Rather than superspectator electrons, a more accurate term for the observed high constant kinetic energy features would be *super-Auger* electrons since the originally excited electron is no longer present to spectate on the process. The ultra-fast charge transfer of electrons from the unoccupied molecular orbitals of the molecule is facilitated by the energetic overlap of all the LUMO states of the core-excited molecule with empty densities of states in the metal surface as shown in Fig. 3b. In addition, while the presented core-hole clock analysis cannot determine an absolute charge transfer timescale, it does however provide evidence for charge transfer on the timescale of the core-hole lifetime indicating that tunnelling of the electrons out of the molecule occurs on a timescale on this order. Ultra-fast charge transfer between an adsorbed molecule and a surface on the low femtosecond timescale is well established in RPES studies,[21, 26, 27, 28, 29, 30, 31] and a similar interpretation involving ultra-fast *bidirectional* charge transfer has also recently been presented for bipyridine molecules adsorbed on the Au(111) surface.[6] Further support for a super-Auger interpretation of the high kinetic energy features is shown in the C_{60}/Ag(111) data (Fig. 5) which extends to photon energies far above the ionisation threshold. The kinetic energy of the super-Auger features are observed to track perfectly linearly with photon energy with no observable spectator shift that would be expected to be present below and not present above the ionisation threshold where the electron is no longer localised on the molecule. It seems reasonable to conclude that the core-hole decay channel that gives rise to these high kinetic energy features involving charge transfer from the surface into the molecule is accompanied by ultra-fast charge transfer out of the molecule to the surface.

However, while this interpreation requires charge transfer from the LUMO states into the surface to occur on the timescale of the core-hole lifetime, there is no strict requirement on the timescale of charge transfer from the surface into the LUMO - all that is required is that there is an electron in the LUMO available during the core-hole decay. This requires an energetic overlap of the LUMO with the filled states in the surface. The energy level alignments shown in Fig. 3b and Fig. 6 show that the LUMO of the C_{60} molecule crosses the Fermi edge of the surface and thus overlaps the occupied densities of states in both the Au(111) and Ag(111) surfaces. However, XAS measures only the unoccupied molecular orbitals in the core-excited state where excitonic effects have been shown to lower the energy of the LUMO states sometimes significantly.[32, 18] It is therefore possible for a molecule LUMO to be located above the Fermi level and to be pulled down below the Fermi level only in the core-excited state. In this case the charge transfer from the surface into the LUMO that gives rise to the super-Auger channels that we observe would need to take place on the low femtosecond timescale, comparable to the core-hole lifetime. Charge transfer from the surface into a molecule is likely to be a much slower process than from the molecule into the conduction band of a surface. This is due to vastly more conduction band states than molecular states, when the electron transfers into the surface, coherence with the initial state is lost on a timescale of 10 fs, compared with transfers of the order 100 fs in the reverse direction.[27, 33, 34] In an early RPES study, neutralization of the core-excited state of N_2 on graphite was shown to occur by charge transfer screening from the substrate into the LUMO of the molecule on the timescale of the core-hole lifetime[7] and in a recent RPES study ultra-fast charge transfer into the LUMO of bipyridine molecules on graphene surfaces was observed[6]. It is therefore possible for the charge transfer processes responsible for the super-Auger decay channel in the present data to occur on the timescale of the core-hole lifetime.

On the other hand, in the case of C_{60} several studies have reported charge transfer already in the ground state associated with the chemisorption, showing a varying degree of charge transfer between the C_{60} molecule and the surface during bonding to the metal surface.[8, 9, 10, 11, 12, 13, 14, 15] The C 1*s* X-ray absorption shown in Fig. 3b closely matches in both energies and intensities that of the C_{60} multilayer in Fig. 2b. This suggests a relatively small amount of charge transfer into the molecule during binding to the surface, which is consistent with previous results that found a charge transfer from Au(111) of 0.8-1.0 electrons per C_{60} molecule.[14, 8] The C 1*s* RPES data for Ag(111) shown in Fig. 5 exhibits three well-defined, narrow and relatively intense lines corresponding the same Core/LUMO/Valence transitions as discussed for Au(111). The fact that these are much more easily measured for the Ag(111) surface than Au(111) suggests that these channels are more populated. This would be consistent with the transfer of more electrons to the molecule than on the Au(111) surface. The C 1*s* XAS shown in Fig. 6 qualitatively supports a higher degree of electron transfer into the LUMO since the relative intensity of the LUMO is weaker than either the multilayer or the C_{60}/Au(111) monolayer, reflecting a lower unoccupied density of states. It would seem reasonable to conclude that there is sufficient overlap of the LUMO of C_{60} with the valence states of the gold and silver surfaces to facilitate charge transfer into the LUMO already in the ground state even if the energy of the LUMO in the core-excited state is lowered due to the creation of a core-LUMO exciton. This would imply that the effect of the core-LUMO exciton on the binding energy of the LUMO is limited to around 0.3 eV otherwise no appreciable overlap between this level and the occupied states of the surface would be present in the ground state to enable charge transfer. This would imply efficient screening of the core-hole by the metal surface or that the LUMO is pinned to the Fermi level of the substrate.

The most significant result from the Ag(111) data shown in (Fig. 5) is the presence of a fourth, even higher kinetic energy super-Auger feature that tracks back to the binding energy of the LUMO at the LUMO resonance. The process requires two electrons to be present in the LUMO to participate in the core-hole decay as illustrated in Fig. 1f. Two LUMO electrons are required to drive this Core/LUMO/LUMO Auger-like transition at all photon energies. The originally photoexcited electron is not shown in the scheme since we assume that it tunnels into the conduction band and plays no further role. The extent of charge transfer from silver to adsorbed C_{60} is debated. The bond to polycrystalline Ag has been shown to be ionic with a charge transfer of 1.7 ± 0.2 electrons per molecule via ultra-violet photoelectron spectroscopy (UPS).[8] Combined UPS/XPS experiments performed on single crystal Ag(111) also assumed an ionic coupling but with only 0.7 electrons involved in the charge transfer.[9] Other experiments using XAS have reported a covalent nature to the C_{60}-Ag(111) bond due to some degree of hybridization between the two highest molecular orbitals and the valence band of the surface.[18] A hybridization between the HOMO-1 of the molecule and the Ag $4d$ state of the surface has also been reported.[10] The adsorption of monolayer C_{60} on Ag(111) has been shown experimentally and theoretically to induce a surface reconstruction stabilised by the stronger C_{60}-Ag interaction than for Au(111).[25] While there are significant differences in the estimated degree of electron transfer from different studies, the observation of the fourth super-Auger feature in (Fig. 5) strongly suggests that the amount of electron charge transfer from the silver surface into the LUMO must certainly be more than one electron (see Fig. 1f).

By integrating the intensities over the four super-Auger lines observed in Fig. 5 in the photon energy region from 305-310 eV at constant kinetic energy we can obtain the intensity of the LUMO-related peak in the resonant Auger relative to those associated with the HOMO, HOMO-1 and HOMO-2 orbitals. The resulting spectrum has been converted to binding energy by extrapolating back to the binding energy positions at the LUMO resonance and is shown in Fig. 10. The high binding energy peaks in Fig. 10 shown as faded components are based on the Auger region of the multilayer data from Fig. 2 and are included only as an aid to obtaining more accurate fits of the HOMO-1, HOMO and LUMO components, and were adjusted so the HOMO-1:HOMO was fixed at the expected 1.8:1 ratio for the C_{60} molecule.[35] If we assume that the intensities of the features associated with super-Auger decay from the HOMO, HOMO-1 and HOMO-2 orbitals are a result only of the occupation of each molecular orbital and not due to any matrix element effects in the transition probability we can infer the relative occupation of the LUMO state and thus the degree of charge transfer from the surface. The intensity of the LUMO-derived super-Auger peak is $(24 \pm 3)\%$ of the HOMO-derived peak. Based on a HOMO occupation of 10 electrons, this result suggests that 2.4 ± 0.3 electrons on average are transferred from the Ag(111) surface to each C_{60} molecule.

The adsorption of C_{60} to the Cu(111) surface is also thought to be ionic with differing degrees of charge transfer reported. Valence band photoemission and XAS data have estimated the charge transfer at 1.5-2 electrons per molecule.[12] A more recent STM and STS study indicated a 3 electron transfer to the molecule.[13] while another photoemission study estimates a charge transfer of 1.6 electrons per molecule.[14] Our photoemission and XAS data clearly show a significant degree of charge transfer, however no super-Auger features were observed in the RPES data. We attribute this to the profound change in the unoccupied molecular orbitals clearly observed in the XAS of Fig. 8b resulting in broad molecular orbital features.

In the case of C_{60} adsorption on Pt(111) the interaction with the surface is even stronger and molecular orbital peaks in both the occupied and unoccupied density of states shown in Fig. 9 are profoundly modified compared to the multilayer due to stronger band hybridisation leading to a surface interaction more covalent in character. Again, no super-Auger decay channels were observed for this surface. It has also been shown that even moderate temperatures can induced polymerisation and decomposition of C_{60} on Pt(111) which might complicate the situation on this surface.[36, 11]

It is also worth noting that on all the surfaces studied the bonding geometry and adsorption sites for the C_{60} molecules may play an important role in the alignment of the molecular orbitals relative to the substrate densities of states. It would therefore be interesting to investigate the super-Auger channels in the RPES of different surface orientations and modified fullerenes molecules.

5. Conclusion

Resonant photoelectron spectroscopy at the C 1*s* absorption edge for C_{60} monolayers adsorbed on Au(111) and Ag(111) surfaces exhibit high constant kinetic energy Auger-like features associated with Auger decay of the core-hole via a transition involving electrons charge transferred from the metal surface into the LUMO of the molecule and therefore referred to as super-Auger electrons. The presence of three super-Auger channels for the C_{60}/Au(111) monolayer corresponding to the Core/LUMO/HOMO, Core/LUMO/HOMO-1 and Core/LUMO/HOMO-2 super-Auger transitions suggests that only one electron is transferred to the LUMO since the channel associated with the Core/LUMO/LUMO transition is not observed. This channel is however observed for the C_{60}/Ag(111) monolayer and by comparing the intensities of the Core/LUMO/LUMO and Core/LUMO/HOMO super-Auger channels we are able to estimate the degree of charge transfer from the silver surface states into the C_{60} LUMO to be 2.4 ± 0.3 electrons on average for each C_{60} molecule. For systems in which more than one electron is transferred thus opening the LUMO-derived super-Auger channel in the RPES data, the degree of charge transfer can be inferred from the relative abundance of each channel. This approach is applicable to a large number of molecule-surface combinations in which significant charge transfer takes place upon adsorption. In contrast, monolayers of C_{60} on the surfaces of Cu(111) and Pt(111) do not exhibit these core-hole decay features in any resolvable way due to the stronger molecule-surface interactions and the substantial modification of the molecular orbitals.

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