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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 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.

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 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,

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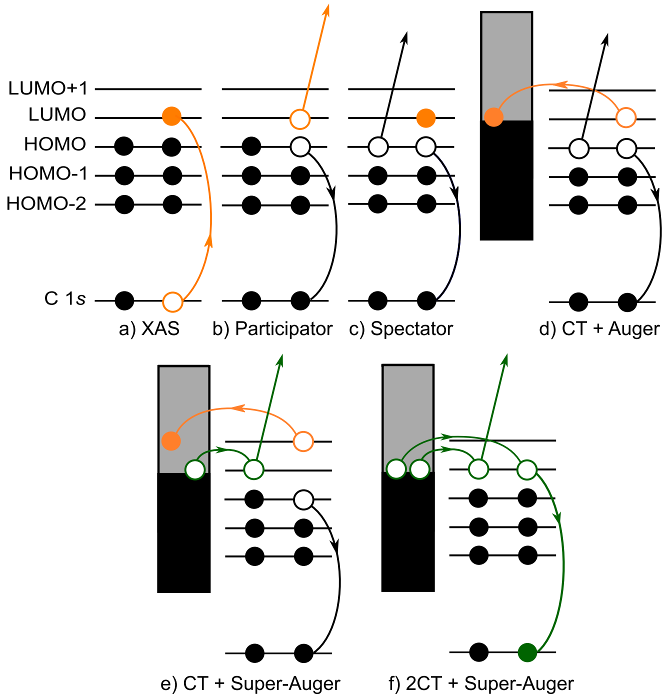

Fig. 1. Schematic illustration of the key electron excitation and subsequent core-hole decay processes observed for a molecule adsorbed on a metallic surface and relevant charge transfer interactions. (a) XAS excitation of a core-level electron (orange) into an unoccupied molecular orbital, in this case 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). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

or for the clean surface itself confirming that the core-hole decay process arises directly from the molecule–surface interaction. Similarly 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 ultra-fast 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 tunnelling 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 than 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 1*s* 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 super-spectator 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 [8–15], 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.

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, followed 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