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Filled and empty states of alkanethiol monolayer on Au (1 1 1): Fermi level asymmetry and implications for electron transport

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ABSTRACT

The electronic structure of the prototypical self-assembled monolayer (SAM) system, i.e. alkanethiol molecules on Au, is investigated via ultraviolet and inverse photoemission spectroscopy measurements. The determination of the density of filled and empty states of the system reveals that the metal Fermi level is significantly closer to the lowest unoccupied molecular orbital (LUMO) of the molecules than to their highest occupied molecular orbital (HOMO). The results suggest that charge carrier tunneling is controlled by the LUMO, rather than by the HOMO, in contrast to what is commonly assumed.

Self-assembled monolayers (SAMs) have received considerable attention for many years due to their importance in the functionalization, passivation and other chemical and structural modifications of numerous surfaces, and to their convenient and inexpensive preparation. Applications of SAMs include control of friction, stiction and wettability [1–3], surface passivation and chemical resistance [4], chemical sensors [5], solar cells [6–8], and micro-/nano-structure fabrication [9].

Alkanethiol molecules, self-assembled on Au, are some of the most extensively studied SAMs due to their ease of preparation, dense packing and good ordering. As a result, alkanethiols on Au have been commonly used as test-bed for investigating processes of charge transport in/through organic monolayers. It is generally thought that charge transport through alkanethiol SAMs occurs mainly via non-resonant tunneling, involving either the highest occupied or lowest unoccupied molecular orbital (HOMO or LUMO) of the alkyl chain [10,11].

Strictly speaking, HOMO and LUMO are concepts adapted from a single molecule gas phase model. While this nomenclature is commonly used for 'thicker' molecular films, we deal here with a monolayer chemically bound to a substrate. Therefore, in the remaining of the text, we refer to these levels as HOSO and LUSO, highest occupied and lowest unoccupied system orbital [12], similar to the HOMO* and LUMO* defined by Engelkes et al. [13].

As a first order approximation, the tunneling barrier height is the energy difference between the Fermi level of the electrode and the closest molecular orbital (E_F – HOSO or LUSO – E_F) [14]. Various techniques have been used to investigate charge transport properties in this system, including nanopores [10], conducting-probe atomic force microscopy [11,15–18], scanning tunneling microscopy [19–21], mercury drop electrode [12,22–24], and large-area molecular junction [24]. Interestingly, these different techniques have produced tunnel barriers within a relatively narrow energy range of ~1.3 to ~2.7 eV [10,11,15–18,20,25]. It has been suggested by several groups that in this system the Fermi level is closer to the HOSO than to the LUSO of the molecule [13,16,25–27]. This is, however, in sharp contrast to the (E_F – HOSO) energy difference of ~4.6 eV that is determined experimentally by ultraviolet photoelectron spectroscopy (UPS) [28]. To date, the energy level alignment in this system remains an unresolved issue, and, thus, also the issue of what is the dominant tunneling mechanism [13,26,27].

In the present work, a combination of UPS and inverse photoemission spectroscopy (IPES) measurements is used to show that the Fermi level in the 1-Octadecanethiol (C18) SAM on Au system is actually significantly closer to the molecular LUSO, implying that charge transport is dominated by electron tunneling with a barrier defined by the LUSO position, relative to the Fermi level. While the UPS/IPES measurements can only be performed on SAMs attached to one electrode, i.e. without a top contact on the molecules, we assume that the energy level alignment between the molecules and the substrate does not change for the monolayer sandwiched between two identical electrodes. We base this assumption on two main points: (i) the electronic structure of the SAM/Au substrate interface is dominated by the relatively strong Au–S chemical bond; (ii) density functional theory (DFT) studies, which indicate that the electronic effect of the substrate (or of the top electrode) decays exponentially into the alkyl chain. Beyond 2–4 carbons away from the interface, the HOMO–LUMO gap of the molecule is fully developed [29,30]. Since our SAMs consist of 18-carbon chains, it is reasonable to assume that the addition of a top electrode will not have a substantial effect on the anchoring part of the molecule (Figure 1).

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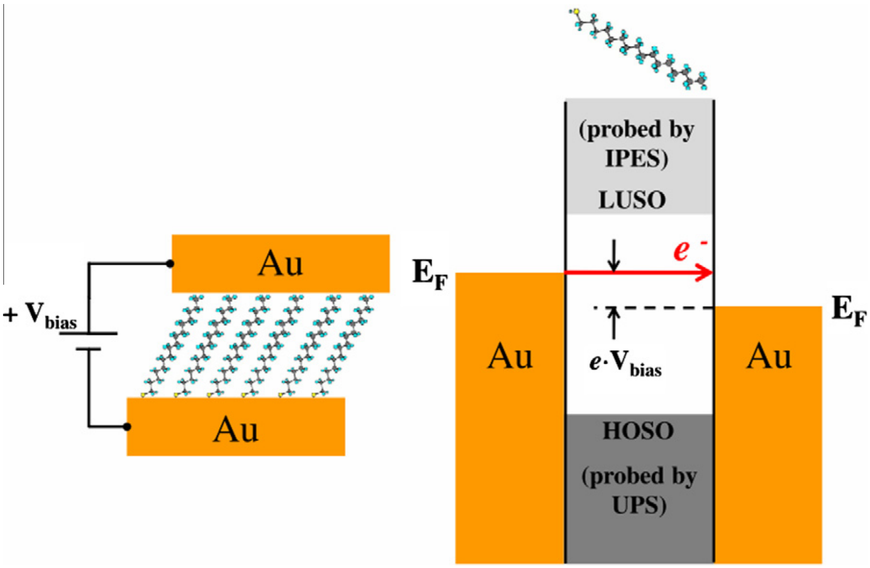

Figure 1. (left) Schematic of a metal/alkanethiol SAM/metal junction; (right) energy diagram that comprises the basic elements deduced from the direct and inverse photoemission measurements performed in this work: (i) the Fermi level of the electrode is significantly closer to the empty states of the molecule than to the filled states; (ii) electron tunneling is controlled by the barrier to the empty states. Filled and empty states of the SAM are represented in dark and light grey, respectively.

The 40 nm Au (99.99%) films were prepared by e-beam evaporation, with a deposition rate of 0.05 nm/s on top of 2 nm Cr on Si. The Cr serves as an adhesion layer between the gold and the Si. The Si substrates were cleaned before evaporation by piranha solution for 30 min, followed by copious rinsing with double distilled water (DDW) followed by sonication in ethanol and drying with N_2. The gold-coated Si wafers were cleaned with a 20 min UV/ozone treatment followed by a 20 min immersion in ethanol. The 1-Octadecanethiol (C18) SAMs were prepared by immersion of the freshly prepared metallic substrates into a 1 mM solution in ethanol at room temperature for 24 h. After removal from the solution, the samples were carefully rinsed with pure ethanol and blown dry with nitrogen.

The samples were transferred to an ultra-high vacuum (UHV) system with only a brief ambient exposure (<1 min). UPS was performed with both He I (21.22 eV) and He II (40.81 eV) lines from a He discharge lamp. A sample bias of −5 V was used during UPS measurements. Pass energies for UPS He I and He II measurements were 5 and 10 eV, respectively. While the signal-to-noise ratio is significantly higher in He I than in He II [31], the probing depth is smaller in He II (~1–1.5 nm) than in He I (1.5–2 nm), which eases discrimination between surface and sub-surface features. Acquiring both He I and He II spectra also helps eliminate possible complications caused by weak parasitic lines emitted from the He discharge lamp (e.g. He I′ at 23.09 eV). To improve the signal-to-noise ratio and reduce radiation damage in IPES [32], measurements were performed at nine different locations on the sample and averaged. Following IPES, UPS measurements were performed again on the same samples to assess the beam damage. The energy resolution in UPS and IPES measurements was 0.15 and 0.45 eV, respectively. Multiple samples, prepared under the same conditions, were measured, and good reproducibility was observed. In UPS measurements, at least two locations on each sample were measured, and good reproducibility was observed. The position of the Fermi level was determined in UPS (both He I and He II) and IPES prior to the measurements with the SAMs, by measuring the Fermi step of a bare Au surface in electrical contact with the investigated sample. The position of the vacuum level, E_{vac}, was defined as well in a standard way, using the onset of photoemission obtained in the He I UPS experiment.

Figure 2a shows the UPS He I spectrum measured on the C18/Au sample. The x-axis is the binding energy with respect to the Fermi level position, which is determined by measuring the Fermi step on a clean Au sample. Based on the position of the photoemission cut-off (−17.15 eV marked in Figure 2a), the work function of the C18/Au sample is determined to be 4.05 eV, which is ~0.2 eV higher

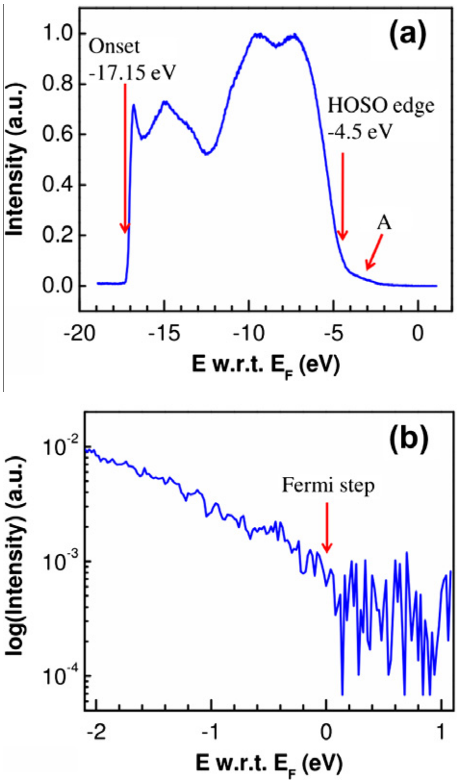

Figure 2. (a) UPS He I spectrum of a C18 alkanethiol SAM on Au, showing the photoemission cut-off at −17.15 eV, the HOSO edge and the feature 'A'. (b) Expanded view of the photoemission region around the Au Fermi edge (marked by an arrow) in a semi-log plot.