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Work Function Pinning at Metal−Organic Interfaces

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Substantial dipoles are formed at interfaces between metals and organic molecules, even in case of relatively weak interactions. We monitor interface dipoles by first-principles calculations of work function changes caused by adsorption of perylene and 3,4,9,10-perylene-tetra-carboxylic-dianhydride monolayers. These changes are the result of two competing effects. Pauli repulsion pushes electrons into the surface, which decreases the work function. If the metal work function is sufficiently low, electrons are donated back from the surface to the molecule. In this regime the work function is effectively determined by pinning of the Fermi level at a molecular energy level.

Introduction

The rapidly developing field of organic electronics has stimulated intensive research into the fundamental electronic properties of molecular organic semiconductors and their interfaces with metal electrodes.[1,2] As the quality of molecular crystals increases, transport of charge carriers across the interfaces between metal electrodes and the organic material starts to determine the device performance.[3,4] Often large dipoles are found at metal−organic interfaces (MOIs), which strongly influence the barrier for charge carrier injection.[5,6] MOI dipoles are localized foremost at the first molecular layer and can be extracted from the change in the surface work function after deposition of an organic monolayer.[2]

The large size of the MOI dipoles indicates a substantial charge reordering at the interface. Obviously this happens if chemical bond formation occurs between the molecules and the metal substrate, as is typically found in self-assembled monolayers.[7−9] More surprising is the observation of large interface dipoles even if the bonding between the metal surface and the molecular layer is relatively weak. Physisorption of inert atoms and small molecules always decreases the metal work function, which is usually called the "pillow effect".[10,11] Most puzzling is the physisorption of π-conjugated molecules, which can lead to a substantial increase, as well as a decrease of the metal work function.[2,5,6]

In this paper we use density functional theory (DFT) calculations to study the work function change due to monolayers of the molecules PTCDA (3,4,9,10-perylene-tetra-carboxylic-dianhydride) and perylene, adsorbed on metal surfaces with work functions ranging from 3.0 (Ca) to 5.3 eV (Au). For both molecules we find a crossover from a regime in which the work function is reduced by the pillow effect to a regime in which the work function is pinned. The pinning value of the work function is ∼4.7 eV for systems with PTCDA overlayers and ∼3.7 for systems with perylene overlayers. Work function pinning is interpreted in terms of charge transfer to the lowest unoccupied molecular orbital (LUMO). The pinning value is relatively constant over a range of distances between the molecular layer and the substrate, which can be explained with a simple model suggesting that the results are quite general. If the metal work function is very low, the LUMO is completely filled and the work function becomes unpinned again.

Computational Details

Density functional theory (DFT) calculations are carried out using the VASP program,[12,13] with projector augmented waves (PAW),[14] a plane wave basis set and the GGA-PW91 or LDA functionals. We use supercells containing a slab of at least three layers of metal atoms, a molecular monolayer adsorbed on one side of the slab, and a vacuum region of at least 10 Å. The geometry of the molecule and of the top surface layer are optimized. The surface Brillouin zone is sampled by a 5 × 5 k-point grid; the plane wave kinetic energy cutoff is 400 eV. To avoid interactions between periodic images of the slab, a dipole correction is applied.[15] Work functions are calculated as in ref 16. Calculated work functions of clean metal surfaces are usually within ∼0.2 eV of the experimental values.

PTCDA adsorbed on noble metal (111) surfaces are experimental model systems for studying MOIs.[17−22] In a monolayer the PTCDA molecules are arranged in a herringbone structure with their planes parallel to the surface, see Figure 1, with experimental molecule-surface distances of 2.86 and 3.27 Å for Ag(111) and Au(111), respectively.[17,20] Common DFT functionals describe strong chemical interactions well, but they fail to capture weaker (such as van der Waals) bonding correctly, resulting in uncertainties in molecule−surface equilibrium distances and binding energies. Using the LDA functional, we
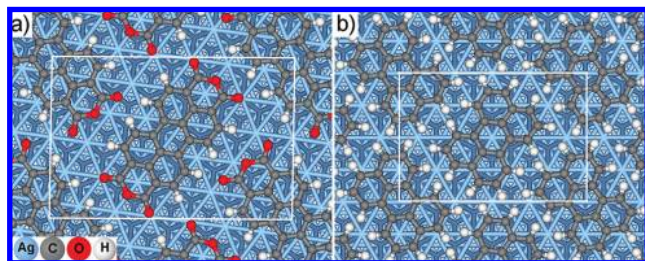
* To whom correspondence should be addressed. E-mail: g.brocks@tnw.utwente.nl.
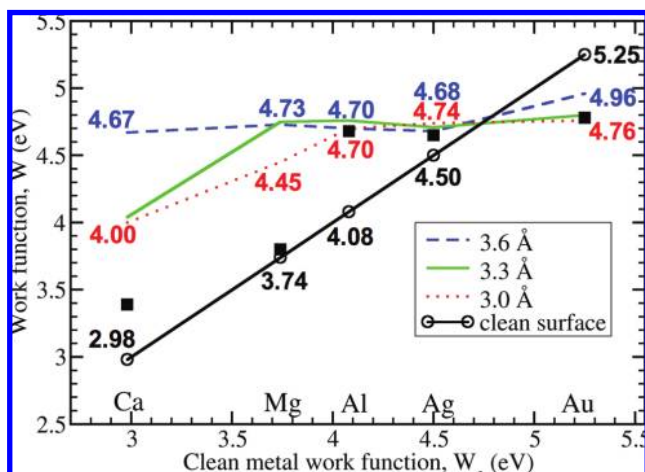† University of Twente.
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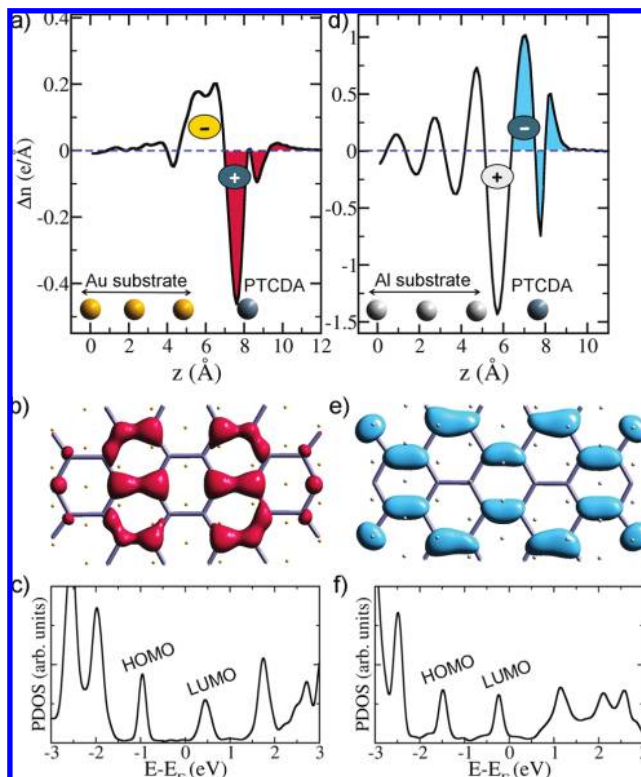**Figure 1.** Herringbone structure of a monolayer of (a) PTCDA and (b) perylene on Ag(111).

Figure 2. Work functions W of a PTCDA monolayer on (111) metal surfaces [(0001) for Mg] with respect to the clean metal work function W_c. The numbers are the calculated values, and the lines guide the eye. The bottom (black) curve refers to the clean metal surfaces. The top three curves are for different molecule−surface distances d. The squares give the values for LDA-optimized molecule−surface distances (see text).

Figure 3. (a) Electron density difference per molecule Δn for PTCDA on Au(111) at $d = 3.3$ Å, as function of z, integrated over x,y. The $\pm$ indicates the direction of the interface dipole; (b) isodensity surface of Δn close to the molecular plane; (c) projected density of states (PDOS) on PTCDA; (d) Δn for PTCDA on Al(111) at $d = 3.0$ Å; (e) isodensity surface; (f) PDOS; labels refer to the same peaks as in (c).

get reasonable molecule-surface distances of 2.75 and 3.15 Å for Ag(111) and Au(111), respectively. The corresponding binding energies are excessively high, however, i.e., 3.0[18] and 1.7 eV/molecule, respectively, consistent with the intermolecular overbinding that is commonly obtained with LDA. In contrast, the GGA-PW91 functional leads to underbinding with equilibrium distances $\gtrsim 3.5$ Å and binding energies $\lesssim 0.1$ eV/molecule.

Despite the problems in obtaining the correct equilibrium geometry in weakly bonded systems, given that geometry, DFT calculations give accurate charge distributions and, therefore, accurate work functions.[18,23,24] Charge distributions are mainly determined by electrostatics and short-range exchange-correlation, which are described well by common DFT functionals. Since GGA calculations give slightly better work functions compared to experiment, we use GGA values in the following.

Results and Discussion

PTCDA Work Function. We perform calculations for a range of distances $d = 3.0$−3.6 Å between molecule and surface, in the range of the experimental values. Figure 2 shows the calculated work functions of a PTCDA monolayer adsorbed on Ca, Mg, Al, Ag, and Au. All metal surfaces are close-packed and the surface unit cells are chosen such that the PTCDA layer has a density of ∼1 molecule per 120 Å². Adsorption of PTCDA on Au decreases the work function, whereas it is increased by adsorption on the other metals. Most remarkably, at distances $d \geq 3.3$ Å, the work function is almost independent of the metal substrate and it is pinned at ∼4.7 eV.

LDA gives short molecule-surface distances, which can serve as lower bounds d_{min}. Optimizing the geometries at d_{min} and calculating the work functions with GGA gives 4.78, 4.65, and 4.68 eV for PTCDA on Au, Ag, and Al(111), respectively, i.e., close to the pinning value in Figure 2. The Ca and Mg surfaces become somewhat unstable at d_{min}; that is, metal atoms are pulled up from the surface, mainly by the carboxyl O atoms, giving metal−O distances in the range 2.3−2.7 Å. This is accompanied by a strong arching distortion of the PTCDA molecule[17] and the work functions are lowered to 3.80 and 3.39 eV for Mg(0001) and Ca(111), respectively. Weakening the molecule−surface interaction by increasing the distance to $d = 3.6$ Å, also brings the work function of PTCDA on Ca and Mg close to the pinning value of 4.7 eV; see Figure 2.

In conclusion, for a range of distances and metal substrates the work function is remarkably constant at ∼4.7 eV. The fact that the work function is pinned by a PTCDA monolayer, as well as the energy of the pinning level, are in good agreement with experimental results.[5,21] "Unpinning" only occurs on very low work function metals, where one expects a strong chemical interaction between molecule and metal.

PTCDA Interface Dipole. The work function change after adsorption results from the formation of an interface dipole. This can be visualized by the (laterally averaged) electron density difference $\Delta n = n_{PTCDA/met} - n_{met} - n_{PTCDA}$, where the electron density of the clean surface n_{met} and that of the isolated molecular layer n_{PTCDA} are obtained in separate calculations. Examples of Δn are given in Figure 3. Calculating the interface dipole as $\Delta\mu = \int z\Delta n(z)\, dz$ gives a good agreement with the interface dipole $e\Delta\mu = \Delta W \varepsilon_0 A$ extracted from the change in work function ΔW (with A the surface area per molecule).

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Figure 3a shows Δn for PTCDA on Au to be localized at the PTCDA/Au interface. The net effect of orthogonalizing the molecular and the surface wave functions, is that electrons are pushed from the molecular region into the metal, called the pillow effect.[11] The resulting dipole layer is localized mainly between the PTCDA layer and the metal surface, and it decreases the work function. Since the pillow effect is sensitive to the overlap between the molecular and the surface wave functions, it decreases with an increasing molecule–surface distance. This is observed in Figure 2 for PTCDA on Au. The charge depletion in the PTCDA region is shown in Figure 3b. Its nodal pattern corresponds to the second highest occupied molecular π orbital of PTCDA. Modeling the interface dipole as a plane capacitor $\Delta\mu = q\delta$ and calculating the charge by integrating over the shaded peak in Figure 3a gives $q = 0.34e$ and $\delta = 1.05$ Å. The latter is much smaller than the molecule-surface distance $d = 3.0$ Å, which illustrates the strong localization of the dipole layer.

The dipole layer generates a potential step that lowers the molecular levels with respect to the Fermi level E_F of the substrate. For PTCDA on Au E_F lies below the LUMO, as is shown in the projected density of states (PDOS) of Figure 3c. The fact that the occupied levels of PTCDA lie substantially below E_F indicates that the charge transfer from the molecular region to the surface is due to the pillow effect, and is not an electron donation from the highest occupied molecular orbital (HOMO) to the metal.

The change in electron density for PTCDA on lower work function metals is qualitatively different. An example for PTCDA on Al is shown in Figure 3d–f. Electrons are transferred from the metal to the molecule. The distribution of Δn is much wider than for PTCDA on Au, although the maximum amplitude is still between the PTCDA layer and the metal surface. Into the Al substrate Δn shows Friedel oscillations that are typical of electrostatic screening in a metal of a charge outside the metal. On the molecule Δn has the nodal structure that is characteristic of the LUMO of PTCDA, indicating that electronic charge has been transferred to the LUMO. This is confirmed by the PDOS in Figure 3f. Indeed experimentally the LUMO is observed at the Fermi level.[17–19,21,22,25]

The Pauli repulsion between the molecular and surface states is operative for adsorption on any metal surface. In general the charge transfer is therefore the net result of pushing metal electrons out of the region of the occupied PTCDA orbitals into the metal (the pillow effect), plus an electron donation from the metal to the LUMO of PTCDA. At the point in Figure 2 where the three upper curves cross the lowest curve (4.7 eV) the work function of a PTCDA covered surface is identical to that of a clean metal surface. At this point the interface dipole is zero and the pillow effect and donation are then exactly balanced. From Figure 2 it can be observed that this point corresponds to the pinning level of the work function.

Pinning at MOIs has been interpreted in terms of a charge neutrality level (CNL), in analogy to a Schottky barrier model for conventional semiconductors.[26,27] The Schottky barrier model relies upon having a large density of interface states (DOIS) in the fundamental gap of the semiconductor, which pins the Fermi level of the metal. Conventional semiconductors such as Si have surface states at or close to the Fermi level, derived from dangling bonds on the surface atoms. Such surfaces are very reactive and bind strongly to metal overlayers, which creates a significant DOIS within the band gap of the semiconductor.[28] In a molecular semiconductor a large DOIS should result from a correspondingly strong metal–molecule interaction, which would lead to a large broadening of the molecular levels. Closed shell molecules usually have a weaker interaction, and most calculations do not give an exceptionally large broadening.[29,30]
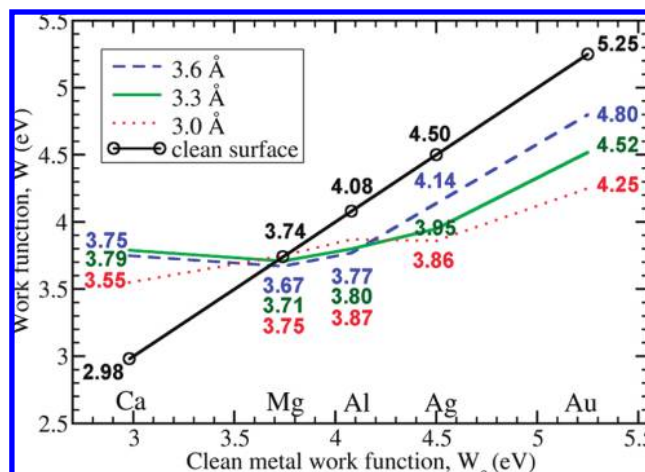

Figure 4. As in Figure 2, for a monolayer of perylene molecules.

In our calculations we also do not observe the very large broadening found in refs 26 and 27; see Figure 3c,f, in agreement with scanning tunneling spectra.[18] Instead we propose that onset of pinning can be interpreted as a balance between the pillow effect and electron donation from the metal to the molecule. On most metals, PTCDA adsorption then leads to a (partial) occupation of the LUMO, as is observed experimentally.[17–19,21,22,25]

Perylene. The position of the LUMO energy level should have a large influence on the charge transfer. To test this we have calculated work functions for adsorbed monolayers of perylene molecules. The electronic structure of perylene is similar to that of PTCDA, but it has a smaller electronegativity, and its levels are shifted upward compared to PTCDA. We use a full monolayer coverage of ~1 perylene molecule per 75–100 Å², see Figure 1. The work function results are shown in Figure 4. Clearly two regimes can be distinguished. For perylene adsorption on high work function metals the pillow effect pushes electrons out of the molecular region into the surface, which reduces the work function. The effect is sensitive to the overlap between the perylene and metal wave functions, which is reflected in the work function changing with the distance between molecule and surface. The analysis of Δn gives a qualitatively similar result to that of PTCDA, see Figure 3. The interface dipole is localized between the metal surface and the perylene layer. The work function of perylene adsorbed on low work function metals is pinned at ~3.7 eV. The analysis of Δn shows a net transfer of electrons from the metal to the LUMO of perylene. For adsorption on Mg the work function is close to that of the clean Mg surface. This marks the point where the pillow effect is exactly balanced by the electron donation from the metal to the LUMO. These two regimes of different work function behavior are also observed for organic layers that are separated from a metal substrate by an (insulating) tunnel barrier.[31]

Model and Conclusions

In the pinning regime the work function is insensitive to the distance between molecule and surface. This seems remarkable as one might expect the interface dipole resulting from this electron transfer to be sensitive to this distance. The latter can be rationalized using a simple phenomenological model of the molecule surface interaction. If one neglects the broadening of the molecular levels alltogether, electrons are transferred from the metal to a molecular energy level. Following Slater's transition state idea, molecular energy levels can be written as

$$\varepsilon_M(N) = \varepsilon_0 + UN$$

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with N the occupation number of the level, U the effective molecular charging energy per added electron, and ε_0 the LUMO energy obtained in a DFT calculation. Slater's transition rule then gives the electron affinity of the molecule as EA $\approx -\varepsilon_M(1/2)$ with U calculated for the isolated molecule.[32] For the PTCDA molecule this gives EA $= 2.98$ eV, in good agreement with the 2.98 eV extracted from a ΔSCF total energy difference calculation.

For a molecule embedded in an adsorbed monolayer, U is renormalized by screening of the molecule by its surroundings. Moreover, as the pillow effect creates an interface dipole that is localized between the surface and the molecules, one has to shift to the molecular levels and replace ε_0 by $\varepsilon_0 - \Delta$, with Δ the potential step induced by the pillow effect. The molecular layer is in equilibrium with the metal substrate, so $\varepsilon_M(N) = E_F$, which determines the occupancy of the molecular level as

$$N = \frac{E_F - \varepsilon_0 - \Delta}{U}$$

The work function of the monolayer covered surface can be written as $W = W_c - \Delta + NF$, with $W_c = -E_F$ the work function of the clean metal surface, and Δ, NF the potential steps induced by the pillow effect and the electron transfer to the LUMO, respectively.[24] Combining the previous equations gives the simple expression

$$W = (W_c - \Delta)\left(1 - \frac{F}{U}\right) - \varepsilon_0\frac{F}{U}$$

If we assume that the electron transfer to the LUMO leads to a charge distribution that can be approximated by a plane capacitor and the molecular charging energy is determined by electrostatics only, then $F = U$,[33] giving the simple expression

$$W = -\varepsilon_0$$

The work function is completely pinned, the pinning level is not affected by the pillow effect, and hence not by the molecule−surface distance.

If $\varepsilon_0 - \Delta > E_F$, then obviously there is no electron transfer to the LUMO. Only the pillow effect is operative and the work function is given by $W = W_c - \Delta$, which restores the sensitivity on the molecule−surface distance. Perylene adsorbed on Au and Ag falls in this regime, as does PTCDA on Au, see Figure 2 and Figure 4. If $\varepsilon_0 - \Delta < E_F$, electrons are transferred to the LUMO, and the work function is pinned, independent of the size of the pillow effect. This is found for perylene on Mg and Ca, and for PTCDA on Ag and Al. If the LUMO is completely filled, the work function becomes unpinned again, as is observed for PTCDA on Mg and Ca at a short molecule-surface distance.

In conclusion, we have calculated the work functions of overlayers of PTCDA and perylene molecules adsorbed on metal surfaces. The pillow effect describes the reduction of the work function if the Fermi level of the metal lies within the HOMO−LUMO gap of the molecules. If the Fermi level crosses a molecular level, the work function is pinned at this level.

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