Dipole formation at metal/PTCDA interfaces: role of the Charge Neutrality Level

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The formation of a metal/PTCDA (3, 4, 9, 10- perylenetetracarboxylic dianhydride) interface barrier is analyzed using weak chemisorption theory. The electronic structure of the uncoupled PTCDA molecule and of the metal surface is calculated. Then, the induced density of interface states is obtained as a function of these two electronic structures and the hopping interaction between both systems. This induced density of states is found to be large enough (even if the metal/PTCDA interaction is weak) for the definition of a Charge Neutrality Level for PTCDA, located $2.45eV$ above the highest occupied molecular orbital. We conclude that the metal/PTCDA interface molecular level alignment is due to the electrostatic dipole created by the charge transfer between the two solids.

Electronic materials made of molecular films are a fast developing field, with many potential applications in organic-based devices. Designing new organic-based materials requires a detailed understanding of the different processes occurring in these devices. In particular, metal/organic and semiconductor/organic interface barriers play a decisive role [1,2]. However, the formation of barriers is not yet well understood.

In the Schottky-Mott model of metal/organic interfaces, it is assumed that no interface dipole is formed at the junction, and that the position of molecular levels with respect to the metal Fermi level is defined by vacuum level alignment. This situation was disproved by Narioka *et al.* [3] who, using ultra-violet photoemission spectroscopy (UPS), found large interface dipoles ($\sim 0.5-1.0eV$) at several metal/organic interfaces. Independent data by Hill *et al.* [4] confirmed this conclusion. Various mechanisms are believed to operate simultaneously at these interfaces, and several models have been advanced [1,2]. Metal-molecule chemical reaction has been seen to create interface gap states that pin the Fermi level [5], a situation that is analogous to that described by the Unified Defect Model proposed for inorganic semiconductor/metal interfaces [6]. Compression of the metal surface electronic tail by adsorbed molecules, leading to vacuum level interface shift, has also been proposed as a general metal/organic interface mechanism [7–9].

In this letter, we explore the first application to a metal/organic interface of the Induced Density of Interface (or virtual) States (IDIS) Model [10]. We study a metal/PTCDA (3, 4, 9, 10- perylenetetracarboxylic dianhydride) interface and analyze how the chemical interaction between the organic molecule and the metal creates an IDIS in the organic energy gap. Our calculations show that, although the chemical interaction is weak, the IDIS is large enough to allow us to define a Charge Neutrality Level (CNL) of the organic molecule. Our results show that the interface Fermi level E_F is pinned at the CNL, a situation similar to that described for the formation of Schottky barriers at conventional semiconductor/metal junctions.

In this theoretical analysis, we study the metal/PTCDA interaction in three steps. First, the molecular orbitals of the organic molecule are calculated using a Density Functional Theory (DFT) local-orbital method [11], care being taken to identify the appropriate wavefunctions associated with the Affinity and Ionization levels defining the molecular transport gap. Then, we calculate the metal/molecule interactions and obtain the electronic density of states in the molecular energy gap. Finally, we define the CNL associated with these states and show that the organic molecule induces an interface dipole strong enough to pin the Fermi level at the CNL. This dipole can be characterized by the parameter

$$S = \frac{dE_F}{d\phi_M}, \tag{1}$$

(where ϕ_M is the metal workfunction), equivalent to the interface slope parameter in the theory of metal/semiconductor junctions [12] and which we find to be 0.2.

In our DFT study of the PTCDA molecule, we use an optimized minimal local orbital basis, and introduce many-body effects by means of the exchange and correlation potential [11],

$$V^{XC}_{i\alpha\sigma} = \frac{\partial E^{XC}[\{n_{j\beta\sigma'}\}]}{\partial n_{i\alpha\sigma}}, \tag{2}$$

where E^{XC} defines the exchange and correlation energy written as a function of the occupation numbers $n_{i\alpha\sigma}$. Typically, the exchange energy is defined by:

$$E^X = -\frac{1}{2}\sum_{i\alpha\sigma} J^{\text{eff}}_{i\alpha} n_{i\alpha\sigma}(1 - n_{i\alpha\sigma}), \tag{3}$$

where $J^{\text{eff}}_{i\alpha}$ is the mean interaction between the charge $n_{i\alpha\sigma}$ and its hole $1 - n_{i\alpha\sigma}$, while

$$E^C = -\frac{1}{2}\sum_{i\alpha\sigma} f_{i\alpha\sigma}\left(\tilde{U}_i - J^{\text{eff}}_{i\alpha}\right) n_{i\alpha\sigma}(1-n_{i\alpha\sigma}), \qquad (4)$$

where $\tilde{U}_i$ is the average intraatomic Coulomb interaction, and $f_{i\alpha\sigma}$ defines the fraction of the exchange hole that is converted into an intraatomic correlation hole [11].

In our actual calculations, we combined a *Fireball* code [13] with the exchange and correlation potential mentioned above. This approach is equivalent to conventional DFT but is especially advantegeous in cases where correlation is important [14], and for calculating the Affinity (A) and Ionization (I) levels of the molecule, as will be seen below in the discussion of Koopman's theorem.

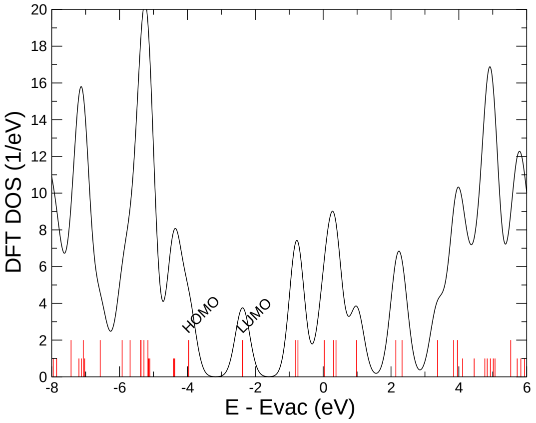

FIG. 1. DFT spectrum (long bars: π states; short bars: σ states) and DOS (introducing a 0.5 eV FWHM Gaussian broadening) for the PTCDA molecule.

Figure 1 shows the spectrum obtained from the DFT calculation; we also calculate a LDOS by introducing for each level a Gaussian broadening with a $0.5eV$ FWHM [15]. This DFT calculation produces a molecular energy gap $\sim 1.6eV$, very small compared to the single-particle gap $A-I$ ($\sim 5eV$) of the isolated molecule [16], and even smaller than the optical gap, $\sim 2.6eV$ [2]. This is due to the fact that the DFT eigenvalues are not directly related to the molecular levels. Note also that, in analyzing the metal/organic interface, one needs to consider the single-particle energy gap of the isolated molecule, $A-I$. At the interface, this energy gap, $A-I$, is reduced by solid-state effects associated with long-range electronic polarization and molecular or lattice relaxations [2,15,17]; these effects will be discussed later.

Let us now consider how to calculate the single-particle gap, $A-I$, for the isolated molecule. We first calculate A and I using the definitions $A = E[N+1] - E[N]$, and $I = E[N] - E[N-1]$, where $E[N_i]$ is the ground-state energy of the molecule with $N+1$, N or $N-1$ electrons. Each case can be calculated using the DFT method described above; we find $I = -5.9eV$ and $A = -1.1eV$, yielding an energy gap of $4.8eV$, in reasonable agreement with the value of $\sim 5eV$ [16]. These calculations tend to give ionization and affinity levels that are too high in energy ($\sim 2eV$) with respect to the experimental evidence. Interestingly, similar results can be obtained using a sort of Koopman's theorem [18], which amounts to introducing an electron (hole) in the LUMO (HOMO) of the molecule, and calculating the total energy of the system *neglecting electron relaxation effects*. In this approach, the Affinity level, for instance, is simply the LUMO level corrected by the following many-body term δA:

$$\delta A = \frac{1}{2}\sum_{i\alpha\sigma\neq j\beta\sigma'} J_{i\alpha,j\beta}\delta n_{i\alpha\sigma}\delta n_{j\beta\sigma'} + \frac{1}{2}\sum_{i\alpha\sigma} J^{\text{eff}}_{i\alpha}\delta n^2_{i\alpha\sigma} + \\ + \frac{1}{2}\sum_{i\alpha\sigma} f_{i\alpha\sigma}\left(\tilde{U}_i - J^{\text{eff}}_{i\alpha}\right)\delta n^2_{i\alpha\sigma}, \qquad (5)$$

where $J_{i\alpha,j\beta}$ is the Coulomb interaction between the orbitals $i\alpha$ and $j\beta$, while $\delta n_{i\alpha\sigma}$ is the change in the occupation number of the orbital $i\alpha\sigma$. A similar equation can be written for δI [18].

This Koopman's theorem approach yields $I = -6.1eV$ and $A = -1.2eV$, in very good agreement with the values given above. This shows that relaxation effects in PTCDA associated with introducing or extracting an electron from the molecule are small, and indicates that the molecular orbitals calculated within DFT for the HOMO and LUMO levels are very appropriate for describing the Ionization and Affinity wavefunctions of the molecule. Note that π and σ orbitals give different values of δA and δI. In our calculations, we obtain the PTCDA energy levels for the molecule by modifying the DFT π and σ levels with the corresponding values of δA and δI given by Koopman's theorem.

Solid-state effects associated with long-range electronic polarization have been analyzed by Tsiper *et al.* [17]. Polarization of molecules of the solid screens the electric field created by the extra charge introduced in the system, either an electron or a hole, modifying the energy levels I and A and the corresponding single-particle energy gap (also called transport gap in the solid). This correction is important, $1-1.5eV$, yet the ionization and affinity wavefunctions of the molecule are not expected to present important modifications. Other effects, such as lattice relaxation and vibronic coupling, only introduce corrections of the order of $0.2eV$, in the transport gap [15].

To summarize the above discussion, the electronic wavefunctions of PTCDA can be described using the results of a DFT approach, introducing a shift in the energy levels. According to independent experimental data [15], we fit this energy gap to a value of $3.2eV$, which seems to include all the effects discussed above.

Finally, we analyze the metal/PTCDA contact using chemisorption theory in the limit of weak interaction between the two solids. Figure 2 shows the geometry of interest: a planar PTCDA molecule located at a distance d from the last metal layer, namely, Au (111).

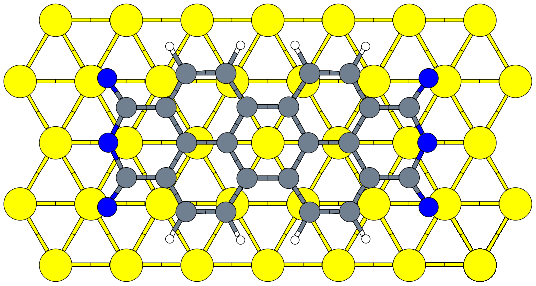

FIG. 2. A PTCDA molecule on a Au(111) surface (Top View). White atoms: H, black: O, dark grey: C, light grey: Au.

We assume the PTCDA wavefunctions, ψ_i, to be described by the DFT method discussed above, and the metal wavefunctions by the DFT-Local Orbital code *Fireball* [13], which also yields the density matrix, $\rho_{\alpha\beta}(E)$, where α and β refer to the local-orbital basis used in the DFT code. In the limit of weak metal-PTCDA interacion [15], the main effect of the metal on the PTCDA electronic structure is to broaden the molecular levels, E_i by a quantity Γ_i given by [19]

$$\Gamma_i = 2\pi \sum_{\nu} |T_{i\nu}|^2 \, \delta(E_\nu - E_i), \tag{6}$$

where $T_{i\nu}$ is the hopping interaction between the molecular orbital ψ_i and the metal eigenfunction, ψ_ν. Equation 6 can be rewritten in a more appropriate way by using a local-orbital basis for the molecule and the metal. With the notation $\psi_i = \sum_j c_{ij}\phi_j$, equation 6 takes the form

$$\Gamma_i = 2\pi \sum_{jj'\alpha\beta} c_{ij}\, T_{j\alpha}\, \rho_{\alpha\beta}(E_i)\, T_{\beta j'}\, c_{j'i}, \tag{7}$$

where the broadening of each molecular level is determined by: (a) the hopping interaction $T_{j\alpha}$ between local orbitals; (b) the coefficients c_{ij} of the molecular orbitals ψ_i; and (c) the density of states matrix of the metal, $\rho_{\alpha\beta}(E_i)$.

Figure 3 shows the hopping interaction between the Au $6s$ orbital and the different orbitals of PTCDA, C $2s$ and $2p$, O $2s$ and $2p$, and H $1s$ (in the following, we neglect the $5d$ and $6p$ orbitals of Au) calculated using a dimer approximation.

Equation 7 can be simplified to a more convenient form by neglecting contributions having $j \neq j'$: these terms represent interference effects between different local orbitals of PTCDA, and tend to cancel each other out. The contribution coming from the Au $6s$ orbitals yields

$$\Gamma_i = 2\pi \sum_{j} |c_{i,j}|^2 |T_{j,6s}|^2 \rho_{6s}(E_i). \tag{8}$$

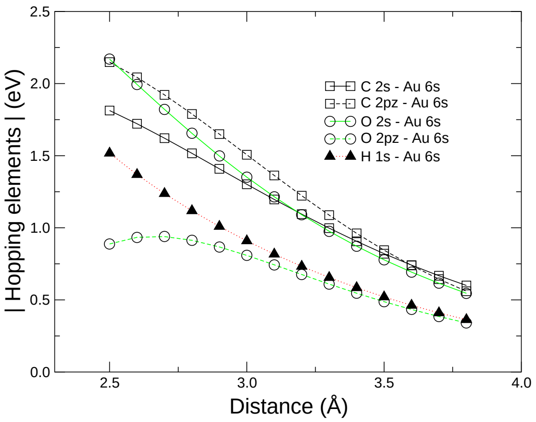

FIG. 3. C, O and H - Au interaction as a function of PTCDA-Au distance.

Each molecular level contributes to the LDOS with the Lorentzian function

$$\frac{1}{\pi}\frac{\Gamma_i/2}{(E-E_i)^2 + (\frac{\Gamma_i}{2})^2}. \tag{9}$$

In our calculations, we find for the π and σ levels around the PTCDA energy gap, $0.3eV < \Gamma_i^\pi < 0.7eV$ and $0.16eV < \Gamma_i^\sigma < 0.37eV$ for Au-PTCDA distances 3.4 Å $< d <$ 3.6 Å. DFT calculations are not reliable for obtaining d, as the metal-PTCDA interaction is of the van der Waals and weak chemical type. We have, however, some indirect information: (i) the distance between planar PTCDA molecules, interacting via van der Waals and weak chemical forces, is $d \sim$ 3.2 Å [20]; (ii) the Au-PTCDA interaction is of the same kind and a little stronger than the PTCDA-PTCDA one [21]; (iii) the atomic radius of Au is $\sim$ 0.5 Å larger than that of C.

From this information, we conclude that the Au-PTCDA distance should be slightly smaller than 3.7 Å = 3.2 Å +0.5 Å, and we calculate Γ_i^π and Γ_i^σ in the range 3.4 Å $< d <$ 3.6 Å. This broadening is in good agreement with the peak widths of π states observed in photoemission experiments [15].

Figure 4 shows the PTCDA LDOS for d = 3.5 Å, $\Gamma_i^\pi = 0.5eV$ and $\Gamma_i^\sigma = 0.25eV$. The energy gap is fitted to $3.2eV$, as mentioned above, and the energy spectrum is rigidly shifted by $\sim 1.2eV$ to fit the HOMO level to its experimental value at the surface of a PTCDA thin film [15]. We also show the CNL, defined as the level yielding charge neutrality conditions in the molecule, and calculate $S = \frac{dE_F}{d\phi_M}$, the interface slope parameter. In our case [12],

$$S = \frac{dE_F}{d\phi_M} = \frac{1}{1 + 4\pi e^2 D(E_F)\delta/A}, \tag{10}$$

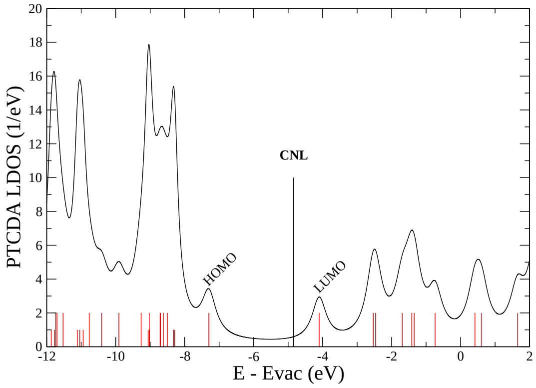

FIG. 4. PTCDA LDOS for the PTCDA/Au(111) interface calculated for $d = 3.5$ Å, $\Gamma_i^\pi = 0.5eV$ and $\Gamma_i^\sigma = 0.25eV$. Long (short) bars correspond to the π (σ) states neglecting the metal-molecule interaction.

where $D(E_F)$ is the PTCDA LDOS (Figure 4) at the Fermi level (practically, the CNL), δ is the distance between the charges induced in the metal and the organic molecule (around 3.5 Å) and A is the area associated with a PTCDA molecule (around 120 Å^2). Our calculation yields $S = 0.2$; it is crucial to mention that this small value of S shows that the LDOS induced in the molecule is high enough (even if the metal/PTCDA interaction is small) to strongly pin the interface Fermi energy close to the CNL.

For the purpose of comparison with experimental data [2], we stress that our CNL is located around $2.45eV$ above the center of the HOMO level of the molecule, in very good agreement with the experimental E_F pinning position. Our calculated value of $S = 0.2$ is a little too large as compared to the value inferred from experiment, $S \cong 0$ [2]. However, our calculations are based on a single case (Au), and a more detailed analysis including other metals should be done. The important outcome of our analysis is that the calculated value of $S = 0.2$ is indicative of a significant DOS at the metal/PTCDA interface, in spite of the weak interaction between the two materials (see Figure 3). This indicates that the interface Fermi level should be close to the CNL (in our calculations, E_F lies $\sim 0.04eV$ below the CNL). The mechanism associated with the formation of the interface barrier is the charge transfer that creates an electrostatic interface dipole, which tends to align the metal Fermi level and the PTCDA CNL.

In conclusion, we have analyzed the metal/PTCDA interface barrier formation using weak chemisorption theory. The aim of this paper was to explore the importance of the IDIS and its contribution to the interface formation. Our results show that even for Au-PTCDA distances for which the interaction is weak ($d \cong 3.5$ Å), the IDIS is high enough to create an interface dipole that tends to align the Fermi level and the PTCDA CNL. This is measured by the slope parameter, S, that our calculations show to be 0.2.

Within this framework, we conclude that the main mechanism that leads to the formation of the Schottky barrier in metal/PTCDA interfaces is the charge transfer associated with the tunneling of metal electrons through the molecule energy gap. Our results show that the interface Fermi level should be close to the CNL of the molecule, which our calculations place around $2.45eV$ above the HOMO level.

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