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Role of the Charge Neutrality Level at Metal/Organic and Organic/Organic Interfaces

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This paper describes how the concepts of Charge Neutrality Level (CNL) and Induced Density of Interface States (IDIS) can successfully explain the energy level alignment at metal-organic and organic-organic interfaces. We propose that the CNL acts as an effective Fermi level for the organic semiconductor: its partial alignment with the metal Fermi level (in the case of metal-organic interfaces) or with the CNL of the other organic material (at organic heterojunctions) determines the interface properties. We review results for several organic semiconductor interfaces. Non-reactive metal-organic interfaces, even in the absence of chemical reaction or defects, have an intrinsic density of states (DOS) induced in the organic energy gap. As the CNL tends to align with the metal Fermi level, the DOS pins the interface Fermi level near the CNL. Theoretical values for the S parameter and Fermi level are in good quantitative agreement with experiment. At organic heterojunctions, the tendency of the CNLs to align gives rise to a restoring dipole. Our intuitive, yet general, approach is able to reproduce the variety of interface dipoles observed experimentally. We conclude that the CNL and induced DOS are important physical quantities governing the energy level alignment at organic semiconductor interfaces.

KEYWORDS: charge neutrality level, interface states, energy level alignment, metal/organic interface, organic/organic interface, organic semiconductor, injection barrier, interface dipole.

1. Introduction

The field of organic semiconductors has been growing very fast in the last decade [1)]. New devices based on organic materials, such as OLEDs, OTFTs and organic solar cells [2)] have already emerged, and there is a pressing need to fully understand all the basic processes that take place in these devices, in particular at interfaces. Metal-organic interfaces determine the injection barriers at the electrodes, and organic heterojunctions are important in devices consisting of several organic materials: the energy level alignment at these interfaces is therefore an issue of great importance.

The topic of molecular level alignment at organic interfaces has been analyzed both theoretically and experimentally [3-11)]. In this paper we review the influence of the induced Density of States (DOS) at the interface and the concept of Charge Neutrality Level (CNL) on the energy level alignment.

The Induced Density of Interface States (IDIS) model and the theory describing the CNL were originally developed for understanding the Schottky barrier formation and Fermi level pinning at *inorganic* semiconductor interfaces [12-13)]. It describes how the interaction between a metal and a semiconductor creates a DOS which fills the semiconductor energy gap. The CNL acts as the Fermi level of the semiconductor interface, and the Fermi level, once the interface is formed, is pinned by the DOS around the CNL. This IDIS model was later extended to semiconductor heterojunctions [14)] with the concept of alignment of the semiconductor CNLs.

2. Metal-Organic Interfaces

The extension of the concepts of CNL and induced DOS to organic semiconductors can be introduced in the context of metal-organic (MO) interfaces. As is now well known, the vacuum level alignment rule is not applicable, since interface dipoles appear and Fermi level pinning occurs at these interfaces [15-16)]. Mechanism such as chemical reaction, or the existence of defects at the interface, can be responsible for the pinning of the Fermi level. Several theoretical studies have been made [3-9)], dealing mainly with reactive metal-organic interfaces. In two recent papers [10-11)], we analyzed several non-reactive MO interfaces and shown that, even in the absence of defects or chemical reaction, there is an 'intrinsic' DOS induced in the gap of the organic material, which can explain the observed dipoles and Fermi level pinning.

The two-dimensional structure of polycyclic aromatic molecules on metal surfaces shows that the organic molecules generally lie flat on the metal surface [17-19)]. The effect of intermolecular interactions can be neglected, since they only slightly broaden or shift the molecular levels, but do not induce a DOS in the organic gap. Since the Schottky barrier depends on these interface gap states, we can therefore restrict our study to a single organic molecule deposited flat on a metal surface, for which we take Au(111), separated by a distance of 3 Å.

The energy level alignment at MO interfaces depends on the electronic structures of the organic material and of the metal, and on the metal-organic interaction.

The electronic properties of the organic molecule can be calculated from first-principles methods based on the Density Functional Theory (DFT). However, due to their localized nature [1)], charge excitations in organic solids are not correctly described by the DFT eigenvalues. Exciton binding energies are large, so that the optical and transport gaps differ significantly [20-22)]. This complicates the analysis of organic semiconductor interfaces, since the optical gap is more accesible experimentally, but it is the transport gap which is relevant for the charge transport properties. Note also that neither the optical nor the transport gap equals the DFT gap. For non-reactive interfaces, the DFT gap cannot be used directly, and the DFT spectrum needs to be corrected [23)] in order to obtain the transport gap. The transport gap, experimentally measured via electron spectroscopies, ranges from 2.3 to 4.6 eV [22] for the materials investigated here. At the interface, polarization effects due to screening from the surrounding organic molecules and from the metal reduce the transport gap by an additional few 100 meV [24].

The main effect of the interaction with the metal substrate is to broaden the molecular levels. In the limit of weak interaction [25], the broadening Γ_i of each molecular level is

$$\Gamma_i = \sum_k |T_{i,k}|^2 \delta(E_k - E_i), \qquad (1)$$

where $T_{i,k}$ is the hopping interaction between the molecular orbital ψ_i, of energy E_i, and the metal eigenfunction, ψ_k. Equation 1 shows how molecular states are broadened if they are in resonance with the metal DOS (see Fig. 1). Expanding $\psi_i = \sum_j c_{ij}\phi_j$ in the local-orbital basis and neglecting off-diagonal terms, Γ_i can be simplified to:

$$\Gamma_i = \pi \sum_{j,\alpha} |c_{i,j}|^2 |T_{j,\alpha}|^2 \rho_{\alpha,\alpha}(E_i), \qquad (2)$$

and can be calculated from the electronic structure of the organic molecule, $c_{i,j}$, of the metal, $\rho_{\alpha,\alpha}$ (E), and the interaction $T_{j,\alpha}$ between the orbitals of both systems.

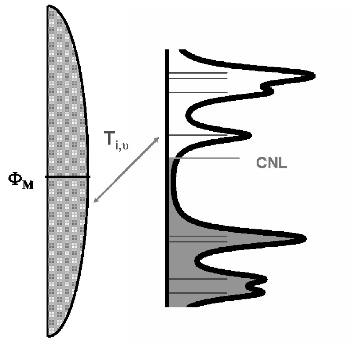

Fig. 1 Broadening of the molecular levels in resonance withthe metal DOS, giving rise to a continuum DOS. The integralof this induced DOS up to the number of occupied states in the isolated molecule (shaded area) determines the position of the CNL.

Due to the interaction with the metal substrate, the organic molecular levels in resonance with the metal DOS are broadened into a Lorentzian function. The initial delta-like distribution for the isolated molecule is transformed into a continuum with, in particular, non-negligible DOS values in the former organic gap. By integrating this induced DOS up to the number of occupied states in the isolated molecule, the position of the CNL is obtained (Fig. 1).

The idea of trying to identify energy levels whose alignment determines the interface properties can be traced back as early as Pauling and Mülliken. Their work was mainly concerned with the quantum properties of atoms, such as explaining the periodic table properties, or the character of chemical bonds, from the quantum properties of the atoms. Consider two atoms, each with its Ionization and Affinity Levels, I_1, A_1 and I_2, A_2. Charge transfer from 1 to 2 depends on the difference I_1 - A_2 (since the electron is removed from I_1 and placed at A_2). Charge transfer in the opposite direction depends on I_2 - A_1. The difference between the two yields $I_1 + A_1$ - ($I_2 + A_2$). Mülliken proposed to consider the average of the atomic Ionization and Affinity Levels, (I+A)/2, as the quantity which determines the charge transfer to or from that atom. The atom with the higher value of (I+A)/2 gains electronic charge from the one with the lower value. Pauling used this idea to determine atom electronegativities [26]. In the present case, considering all molecular states in addition to the HOMO and LUMO is crucial, since, due to the interaction at the interface, these states will have a lorenztian broadening, and several will contribute to the position of the CNL in the organic gap. For several organic materials, the CNL is located close to the LUMO [10,11] as the DOS is higher around the HOMO that around the LUMO. The tails of these states push the CNL upwards in the gap. The simple (I+A)/2 average, on the other hand, predicts the CNL always at midgap.

In semiconductors, our generalization of the (I+A)/2 concept coincides with the average of optical gaps in the Brillouin zone, which is the CNL of the semiconductor. In inorganic semiconductors, the CNL was shown to determine the energy level alignment and dipole formation at metal-semiconductor and semiconductor-semiconductor interfaces [12-14]. By now, the CNL model in inorganic semiconductors is well established. In organic semiconductors, the idea of using the average (I+A)/2 as the chemical potential of the organic material has been recently used by Crispin [27] for a reactive MO interface. The value (I+A)/2 was used to predict (correctly) the direction of charge transfer upon chemisorption. In light of this, our approach for the calculation of the CNL can be viewed as a generalization of the previous (I+A)/2 concept to the case of organic semiconductors, which includes a realistic representation of the molecular levels around the HOMO and the LUMO. Our results for MO and OO interfaces yields results for Fermi levels and interface dipoles in good agreement with experiment, suggesting that including the effect of many molecular levels is necessary for the calculation of the CNL.

The role of the CNL is that of an effective organic Fermi level of the organic material, which tends to align with the metal Fermi level, E_F^{metal}. The relative position of the CNL and E_F^{metal} (when referred to a common vacuum level) determines the direction and magnitude of the charge transfer between the metal and the organic material. This charge transfer creates an interface dipole, Δ, which tends to align the CNL and E_F^{metal}.

We have analyzed the energy level alignment between Au and five different organic semiconductors: 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA), 3,4,9,10 perylenetetracarboxylic bisbenzimidazole (PTCBI), 4,4'-N,N'-dicarbazolyl-biphenyl (CBP), copper phthalocyanine (CuPc) and Pentacene. Our results, summarized in Table I show that our approach using the concept of CNL and induced DOS yields the correct pinning behaviour at these interfaces. The degree of pinning at the interface can be characterized by the parameter, $S = \frac{dE_F}{d\phi_M}$, which gives the dependence of the interface Fermi level position, and thus the injection barrier, on the metal work function, ϕ_M. This screening parameter S can be calculated from our results using:

$$S = \frac{dE_F}{d\phi_M} = \frac{1}{1 + 4\pi e^2 D(E_F)\delta/A}, \tag{3}$$

where $D(E_F)$ is the induced DOS at the Fermi level, δ is the metal-molecule distance and A is the area associated with each organic molecule.

The calculated values of the CNL and S can be used to calculate the theoretical position of the interface Fermi level, E_F:

$$E_{CNL} - E_F = S(E_{CNL} - \phi_M), \tag{4}$$

adopting the convention that the organic levels are fixed, and that the interface dipole acts on the metal, shifting its electronic spectrum.

In our calculations, we have taken ϕ_M = 5.1 eV. Note that the reduction of the metal work function due to the compression of the surface electron wavefunction by the adsorbed organic mlecules (the "pillow" effect 5,8)) can be straightforwardly incorporated into our formalism as a modification in the initial value of ϕ_M.

Table I. Calculated 10,11) and experimental 20) results for the slope parameter, S, and the position of the interface Fermi level, E_F (eV)

	S (theory)	S (exp.)	E_F (theory)	E_F (exp.)
PTCDA/Au	0.13 (d=3.0Å)	0.0	-4.84	-4.8
PTCBI/Au	0.18 (d=3.2Å)	0.0	-4.53	-4.6
CBP/Au	0.5 (d=3.5Å)	0.6	-4.65	-4.48
CuPc/Au	0.25 (d=3.5Å)	0.25	-4.27	-4.3
Pentacene/Au	0.2 (d=3.5Å)	0.37	-4.28	-4.3

So far, we have just considered the case of organic semiconductors deposited on Au. How do these results for the CNL and induced DOS change for other metals? More generally, **is the CNL an intrinsic property of the organic material?** We believe that, although our results do not completely answer this question, they nevertheless suggest that this is the case. Given the large size of these organic molecules, which in many cases form incommensurate lattices 18) on the metal substrate, for any adsorption geometry there are simultaneously several (top, bridge, hollow...) configurations on different parts of the molecule, so that the particular interface geometry does not affect the position of the CNL. We have changed the broadening Γ_i of the molecular levels by factors of up to 2 and found that the position of the CNL remains unchanged. Variations in the metal-organic distance, d, or in the interaction strength, $T_{j,\alpha}$ give rise to changes in the level broadenings, Γ_i. This means that the position of the CNL is insensitive to the details of the interaction, and suggests that it will not change when the organic material is deposited on another metal substrate. It shows that, at least for weakly interacting systems, the CNL is a robust quantity, almost independent of the details of the metal-organic interaction. At reactive metal-organic interfaces, where the interaction is strong 18,28), the interface states induced in the organic gap should be calculated for each particular interface. But even though the CNL scenario presented here is not applicable in these cases, the fact that the Fermi level is completely pinned for PTCDA or PTCBI on **all** metals suggests that the particular shape of the induced DOS does not greatly affect the position of the CNL. More work in this direction will clarify these issues.

For weakly interacting interfaces, the CNL picture offers an attractive proposal, yielding results in good agreement with experiment. Given their weak interaction, this CNL scenario can be extended to organic heterojunctions.

3. Organic-Organic Interfaces

The experimental evidence for organic-organic interfaces 29) presents an intriguing situation: the vacuum level alignment rule is observed in many cases, but some interfaces also exhibit large dipoles (up to 0.5 eV). These dipoles cannot be correlated with the relative positions of the Ionization or Affinity levels of the organic materials. How, then, can the energetics of organic heterojunctions be understood?

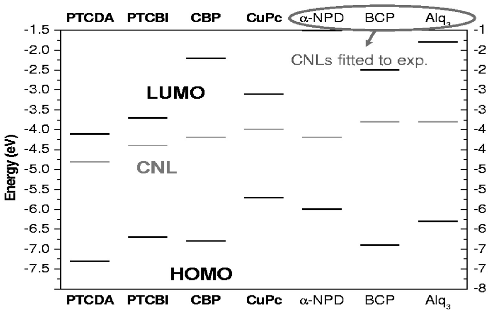

Fig. 2 Position of the CNL (with respect to the vacuum level) for several organic materials. The HOMO and LUMO are shown for comparison. The results for the first four materials have been calculated, whereas those for the last three were fitted to experiment.

Extending the previous CNL ideas, we propose [30] that the energy level alignment at organic heterojunctions is governed by the partial alignment of the CNLs of the two organic materials. The energy difference between the CNLs gives rise to charge transfer between the two organic semiconductors. This creates an interface dipole, which tends to reduce the initial CNL difference. The position of the CNL of several organic materials is shown in Fig. 2. We stress that the CNLs for the first four materials have been calculated as described above, whereas the latter three were obtained from a fit to experimental data [29]. The screening at the OO interface tends to reduce the initial CNL difference. This screening can be characterized by a parameter S [31] similar, but not equal, to the one introduced for MO interfaces, which can be evaluated from the static dielectric functions, ε_i, of the two organic materials:

$$S = \frac{1}{2}\left(\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2}\right), \tag{5}$$

The lack of experimental data for ε_i for the different organic materials complicates the calculation of S using equation 5. We can, however, estimate ε_i, since $(\varepsilon - 1)$ is inversely proportional to the square of the energy gap of the material [13]. We find $0.4 < S < 0.7$, typically $S \approx 0.5$. This means that screening at organic heterojunctions is weak, and that the initial CNL difference is not completely reduced.

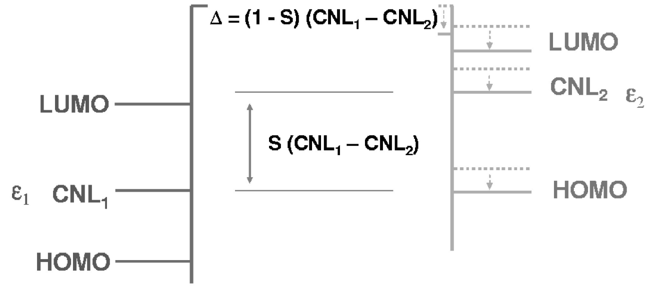

Fig. 3 OO interfaces: the difference $(\mathrm{CNL}_1 - \mathrm{CNL}_2)_{initial}$ gives rise to charge transfer and creates an interface dipole Δ. The initial CNL difference is not completely screened.

When two organic semiconductors are brought together (Fig. 3), charge flows from the one with the higher CNL (ie. less negative) to the one with the lower CNL (more negative). This charge transfer creates an interface dipole which shifts the whole spectrum, including vacuum level, of one organic material (Organic $_2$ in Fig. 3) and screens, though not completely, the initial difference CNL_1 - CNL_2. The final CNL difference is given by

$$(CNL_1 - CNL_2)_{final} = S(CNL_1 - CNL_2)_{initial}, \tag{6}$$

and the magnitude of the interface dipole is

$$\Delta = (1 - S)(CNL_1 - CNL_2)_{initial}, \tag{7}$$

The calculated dipoles are found to be in good agreement with experiment [30]. It should be stressed that, even though these values of Δ were obtained from the estimated ε_i, they depend predominantly on the CNLs, and are not significantly affected by variations in ε_i. As seen in Figure 4, the directions of the calculated dipoles always agree with experiment, and the agreement in magnitude is in most cases within experimental error (0.1 eV).

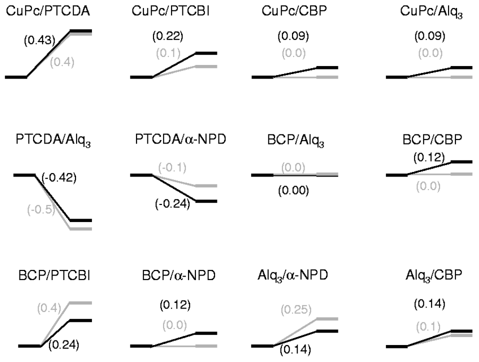

Fig. 4 Calculated [30] (black) and experimental [29] (grey) interface dipoles at several organic heterojunctions. The magnitude of the dipole (in parentheses) is given in eV.

In this way, the apparent contradictory behaviour of organic heterojunctions finds a simple explanation: notice that all the CNLs, except for PTCDA and PTCBI, lie within (4.0 ± 0.2) eV. This means that interfaces between these materials will have a small CNL difference, and will give rise to a small, often negligible, dipole. Interfaces with PTCDA or PTCBI, on the other hand, will have a large initial CNL difference, which results in a large interface dipole.

4. Conclusions

In summary, we have reviewed the role of the CNL and induced DOS at several organic semiconductor interfaces. At interfaces between a non-reactive metal and organic materials, the S parameter is in reasonably good agreement and the calculated interface Fermi level position is in excellent agreement with experiment. At organic heterojunctions, where the interaction is also weak, the CNL picture yields interface dipoles in good agreement with experiment, and explains the apparently contradictory coexistence of the vacuum level rule in most cases with large dipoles in some interfaces. A full understanding of strongly interacting interfaces will need more theoretical work.

The energy level alignment at systems with weak interaction, such as non-reactive MO interfaces and organic heterojunctions, can be succesfully described by the tendency of the organic CNL to align with the metal Fermi level (MO interfaces) or with the CNL of the other organic material (organic heterojunctions). We therefore conclude that the CNL and induced DOS are important quantities, governing the energy level alignment at organic semiconductor interfaces.

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