

# Schottky barrier height at an organic/metal junction: A first-principles study of PTCDA/X ( $X = \text{Al}, \text{Ag}$ ) contacts

S. Picozzi

*Istituto Nazionale di Fisica della Materia (INFM), Dipartimento di Fisica, Univ. L'Aquila, 67010 Coppito, L'Aquila, Italy*

A. Pecchia, M. Gheorghe, A. Di Carlo, and P. Lugli

*Istituto Nazionale di Fisica della Materia (INFM), Dipartimento di Ingegneria Elettronica, Univ. Tor Vergata, 00133 Roma, Italy*

B. Delley

*Paul Scherrer Institut, WHGA/123, Villigen PSI, Switzerland*

M. Elstner

*Department of Physics, University of Paderborn, Germany*

(Received 4 April 2003; revised manuscript received 31 July 2003; published 13 November 2003)

First-principles calculations within the density-functional theory have been performed for a 3,4,9,10 perylene-tetracarboxylic dianhydride (PTCDA) molecule deposited on Al(111) and Ag(111) substrates, focusing on the structural and electronic properties. The relatively large interplanar distance between the PTCDA plane and the Al surface, along with the small adsorption energy, suggest the interaction to be pretty weak. Moreover, the analysis of Mulliken population combined with the density of states shows that the main interactions occur in the molecular anhydride end groups, whereas the perylene core is basically unaffected by the Al substrate. Very similar results are obtained for PTCDA deposited on the Ag(111) surface, the interaction being even weaker than with Al, as expected for the less reactive noble metal. As for the technologically important issue of the potential lineup, our results show that the PTCDA/Al contact has a rectifying character, with a  $p$ -type Schottky barrier height of about 1.5 eV. This same value is obtained for the PTCDA/Ag contact, irrespective of the interface geometry. This suggests that, irrespective of the underlying metal, the Fermi level is pinned at the same energy position with respect to the PTCDA highest occupied molecular orbital, in excellent qualitative agreement with experimental findings.

DOI: 10.1103/PhysRevB.68.195309

PACS number(s): 73.40.Ns, 73.61.Ph, 71.20.Rv

## I. INTRODUCTION

Molecular organic semiconductors are promising materials for electronic and optoelectronic devices, such as organic thin-films transistors<sup>1</sup> and light-emitting diodes,<sup>2</sup> for use in flat-panel display applications. Even though the experimental realization of such devices is currently under way, the physical mechanisms of electronic transport is still largely unknown. One of the critical points in the device performances is the interface between metal contacts and organic materials, whose properties control the balance of electrons and holes injected in the device. Upon adsorption of the molecule on the metal surface, some of the most interesting issues are the following: (i) charge transfer between the molecule and the substrate; (ii) the interaction of the molecular levels with the continuum of states in the metal, and (iii) the lineup of the molecular levels relative to the metal Fermi level. Despite the technological importance of these issues, only a few investigations have so far been focused on the structural, chemical, and electronic properties of metal/organic junctions. In particular, due to the large size of the molecules of technological interest, accurate theoretical studies of the related metal/molecule interfaces have been so far hampered by the high computational cost and only recently first-principles calculations based on density-functional theory have been performed for some of these systems.<sup>3-7</sup>

One of the most promising organic materials for device applications is the 3,4,9,10 perylene-tetracarboxylic dianhydride (PTCDA). Stacked PTCDA molecules form a van der Waals molecular crystal, having a monoclinic bulk crystal structure with the [102] direction perpendicular to the plane of the molecules.<sup>8</sup> In recent years, PTCDA has become a *model* molecule in the investigations of the interactions of functionalized polycyclic aromatic molecules with metal surfaces.<sup>8-13</sup> The interface between PTCDA and Al or Ag is the focus of the present paper. Our simulations are meant to reproduce the interface that may be obtained experimentally by depositing PTCDA on the metal surface. We recall that the interpretation of interfaces formed in the opposite deposition sequence (such as those studied in Refs. 8 and 4 from the experimental and theoretical point of view, respectively) is often complicated by interdiffusion of metal atoms in the organic films.

The work is organized as follows: in Sec. II we give some details about the calculations, in Sec. III we discuss the equilibrium structural properties of the PTCDA/Al interface and the related energetics, in Sec. IV we focus on the electronic properties, in terms of charge transfer, density of states and Schottky barrier heights, of the PTCDA/Al system, in Sec. V we focus on the relevant results for the PTCDA/Ag junction. Finally, in Sec. VI we draw our conclusions.

## II. COMPUTATIONAL DETAILS

Our calculations are performed within the density-functional theory, where the exchange-correlation functional has been parametrized according to the generalized gradient approximation (GGA) in the Perdew-Becke-Ernzerhof (PBE) flavor.<sup>14</sup> Test calculations for the PTCDA/Ag system were also performed using the local-density approximation (LDA).<sup>15</sup>

Dmol<sup>3</sup>, i.e., density-functional theory for molecules and three-dimensional periodic solids (DMol<sup>3</sup>), uses fast convergent three-dimensional numerical integrations to calculate the matrix elements occurring in the Ritz variational method. The basic description of the Dmol code for molecules can be found in Ref. 16, whereas its generalization to three-dimensional periodic solids is explained in Ref. 17. The numerical atomic response basis set is designed to give a maximum of accuracy for a given basis set size. In our calculations, we used a double set of numerical valence functions with the local basis cutoff  $R_c$  of 9.0 a.u. and a  $\mathbf{k}$ -points mesh of 14 points chosen according to the Monkhorst-Pack scheme.<sup>18</sup> The relativistic effects are considered using a pseudopotential scheme.<sup>19</sup> The DMol<sup>3</sup> method was recently and successfully applied to grain boundaries<sup>20</sup> problems and several magnetic semiconductors.<sup>21</sup>

Given the high computational cost involved, some preliminary computations and geometry optimizations were performed using the DFTB code, which is a density-functional based tight-binding formulation for material simulations. The method has been described in detail in Refs. 22 and 23. The key advantage of DFTB is the use of a minimal optimized basis set and the approximation of the density-functional Hamiltonian as a superposition of pair potentials that can be stored in lookup tables.

## III. PTCDA/AL: STRUCTURE AND ENERGETICS

Several experimental works<sup>12</sup> have reported that polycyclic aromatic molecules tend to adsorb on a metal surface in a flat-lying geometry; therefore in all the systems considered during the geometry optimization the adsorbed PTCDA is kept parallel to the metal [111] surface. In particular, we consider three (111) ordered Al layers (each containing 36 atoms) with the cubic experimental lattice constant ( $a_{Al} = 4.05 \text{ \AA}$ ) (Ref. 24) to simulate the metallic substrate, on top of which a single PTCDA molecule is deposited. About 10  $\text{\AA}$  of vacuum in the  $z$  direction are added, in order to simulate the surface. As a result, the unit cell contains 146 atoms. The unit-cell dimensions are large enough to neglect the in-plane interactions between each PTCDA molecule and those in the nearby unit cells. Since each cell contains a single PTCDA molecule, we have neglected the molecular van der Waals interactions leading to the PTCDA molecular crystal experimentally observed; for this same reason, the simulated system is not properly a PTCDA/metal junction, but rather a metal surface with an on-top deposited organic molecule. However, we expect (i) the weak van der Waals forces leading to the molecular crystal not to strongly affect the metal/PTCDA interactions, which we are mainly interested in, and

(ii) the Schottky barrier height, ideally relative to two semi-infinite bulks — PTCDA molecular crystal and metal bulk — to be mainly determined by the interaction of the metal substrate with the first PTCDA monolayer (see below).

The minimization of the *ab initio* forces leads to a small “buckling”  $b$  of the PTCDA atoms (i.e., a vertical displacement with respect to the average  $z$  coordinate of the PTCDA plane) at most equal to 0.2  $\text{\AA}$ .

Using the DFTB code we have scanned a large configuration ensemble for the interface PTCDA/Al. In these calculations we have kept fixed the Al atoms and moved rigidly the PTCDA molecule around, keeping it at a constant distance from the Al surface. The result of these calculations was to find the adsorption configuration which minimizes the total energy of the system, and provide a starting point for a more accurate analysis with DMol<sup>3</sup>.

In Figs. 1(a) and 1(b) we show the top view and side view, respectively, of our PTCDA/Al optimized structure according to DFTB and lately checked with DMol<sup>3</sup>. Figure 1(c) shows the inequivalent atoms within PTCDA. In Table I we report the relevant distances between the atoms of the PTCDA when adsorbed on the metal and the C-O-C angle. The calculated C-H bond length ( $d = 1.09 \text{ \AA}$ ) is close to the corresponding value ( $d = 1.1 \text{ \AA}$ ) in the CH<sub>4</sub> molecule. If compared to the equivalent distances between atoms in the DMol<sup>3</sup> optimized single PTCDA molecule (also reported in Table I), we note that the deviation is at most 1% both on the bond lengths and on the C-O-C angle, giving evidence of small structural modification induced on the molecule by the Al substrate. Moreover, we point out that our DMol<sup>3</sup> optimized distances for the single PTCDA molecule are in excellent agreement with those reported in a recent work performed within density-functional molecular-dynamics simulations performed on Ti impurities within PTCDA,<sup>4</sup> and with available experimental data.<sup>25</sup>

Focusing on the equilibrium distance between the PTCDA plane and the surface Al plane,  $d = 3.45 \text{ \AA}$ , its rather large value suggests that the interaction between PTCDA and Al is weak, to be mostly identified as physisorption rather than chemisorption.

Further insights about the adsorption mechanism can be obtained by evaluating the binding energy, estimated as

$$E_b(\text{PTCDA} - \text{Al}) = E_{tot}(\text{PTCDA} + \text{Al}) - E_{tot}(\text{PTCDA}) - E_{tot}(\text{Al}),$$

where  $E_{tot}(\text{PTCDA} + \text{Al})$ ,  $E_{tot}(\text{PTCDA})$ , and  $E_{tot}(\text{Al})$  denote the total energies of the adsorbed system, of the isolated PTCDA molecule, and of the Al substrate, respectively.

The binding energy vs the interplanar distance  $d$  (and the related parabolic fit around equilibrium conditions) is shown in Fig. 2. Deviations of about 20% around the equilibrium distance  $d$  produce deviations of about 30 meV in the binding energy. Given also the uncertainty deriving from the PTCDA position in the  $x, y$  plane, we therefore estimate a numerical uncertainty on  $E_b$  of about 0.3 eV. The calculated  $E_b$  value is about  $-1.2 \text{ eV}$ ; the negative value suggests that the process is exothermic and therefore energetically stabler than the two separate constituents. The rather small binding

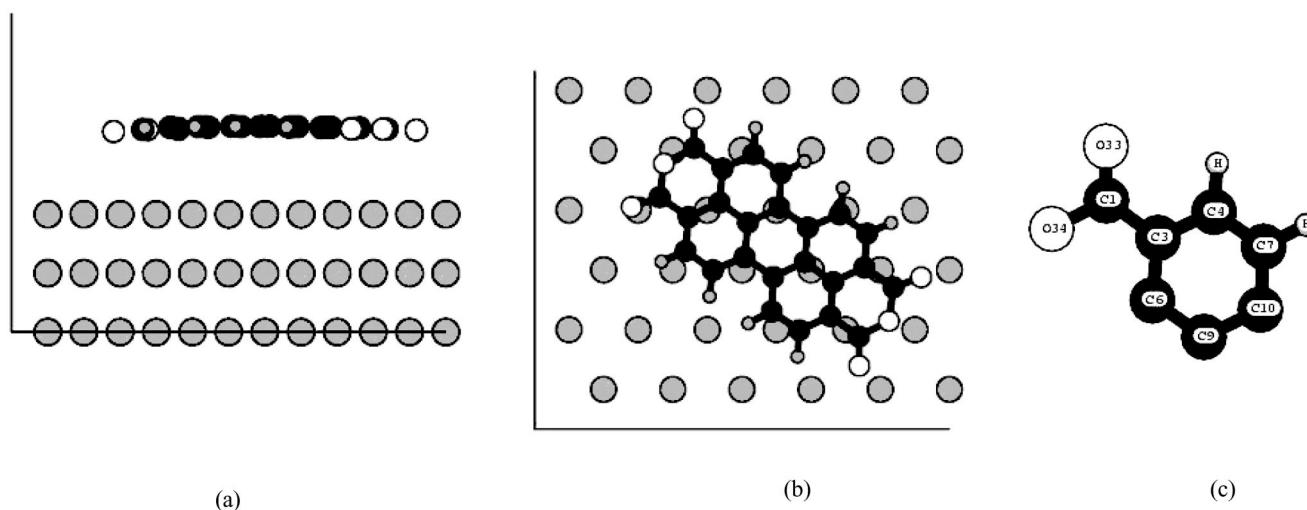


FIG. 1. (a) Side and (b) top view of the adsorbed PTCDA molecule on Al[111] substrate [for the sake of clarity, only the surface Al atoms are shown in panel (b)]. (c) Inequivalent atoms within isolated PTCDA molecule. Small (large) grey circles denote H (Al) atoms; black and white circles denote O and C atoms, respectively.

energy and the shallow minimum shown in Fig. 2 could be partly due to the inability of the present exchange and correlation functional within density-functional theory to accurately describe the long-range dispersion interactions,<sup>26</sup> but, nevertheless, suggests the PTCDA/Al interaction to be pretty weak. In particular, even within the large numerical errors, the rather small value seems to be consistent with the physisorption mechanism previously pointed out.

#### IV. PTCDA/AL: ELECTRONIC PROPERTIES

##### A. Charge transfer and density of states

Let us first address the issue of charge transfer between the molecule and the metal substrate. It is well known that the Mulliken charge analysis<sup>27</sup> of bond population is not quantitatively exact; however, trends of charge transfer within the molecule and upon adsorption on the Al surface are expected to be correctly predicted. In Table II, we report the Mulliken charges in the single molecule ( $Q_M$ ), along with the difference between the Mulliken charges in the single molecule and in the molecule adsorbed on Al ( $\Delta Q_M$ ) on the different PTCDA atoms. As for the isolated molecule, it is clear that there is an appreciable valence charge transfer (as large as 0.4 electrons) from carbon to oxygen atoms in the anhydride groups, reflecting the high electronegativity of O. This is consistent with experimental findings from photo-

TABLE I. Average DMol<sup>3</sup> calculated bond lengths [ $d(\text{C-O})$ ,  $d(\text{C-C})$ ,  $d(\text{C-H})$ , in Å] and C-O-C angle [ $\alpha(\text{C-O-C})$ , in degrees] within the PTCDA: comparison between the single molecule and the molecule adsorbed on Al[111].

|          | $d(\text{C-O})$ | $d(\text{C-C})$ | $d(\text{C-H})$ | $\alpha(\text{C-O-C})$ |
|----------|-----------------|-----------------|-----------------|------------------------|
| Adsorbed | 1.31            | 1.42            | 1.09            | 116.7                  |
| Single   | 1.30            | 1.41            | 1.09            | 117.7                  |
| Expt.    | 1.29            | 1.40            |                 | 118.5                  |

emission spectroscopy on PTCDA films.<sup>8</sup> A significant charge transfer (about 0.3 electrons) is also evident from the H to C atoms. Upon adsorption on Al, we note that there is a negative charge accumulation on the PTCDA molecule: about 0.9 electrons are transferred from the metallic substrate to the organic overlayer. It has to be pointed out that this value might be affected by errors arising from the incorrect position — due to DFT underestimation of excited states, see below — of the lowest unoccupied molecular orbital

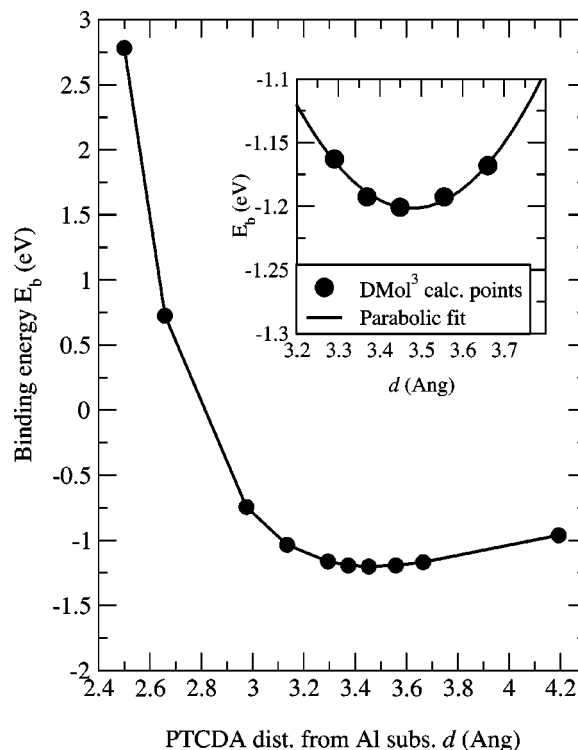


FIG. 2. Main panel: Binding energy of the PTCDA/Al junction (in eV) vs interplanar distance  $d$  (in Å). Inset: Parabolic fit close to the energy minimum (solid line).

TABLE II. Mulliken charges in the single molecule ( $Q_M$ ) and difference between the Mulliken charges in the single molecule and in the molecule adsorbed on Al ( $\Delta Q_M$ ) on the different atoms.

| Atom | $Q_M$ | $\Delta Q_M$ |
|------|-------|--------------|
| C1   | 0.48  | 0.01         |
| C3   | -0.08 | 0.02         |
| C4   | -0.23 | 0.03         |
| C6   | 0.1   | 0.01         |
| C7   | -0.28 | 0.02         |
| C9   | 0.02  | 0.01         |
| C10  | 0.04  | 0.03         |
| O33  | -0.34 | 0.08         |
| O34  | -0.42 | 0.04         |
| H25  | 0.26  | 0.01         |
| H26  | 0.30  | 0.01         |

(LUMO). Within our approximations, Table II shows that the charge transfer leads to a positively charged metal and a negatively charged molecular overlayer, suggesting a kind of electrostatic bond rather than a real chemical bond. The charge transfer is particularly evident in the O atoms in the anhydride groups; on the other hand, the inner C atoms are almost unaltered compared to the PTCDA isolated configuration. This shows that the main interaction between substrate and molecule occur in the molecular end groups, as expected from the electrophilic character of O, whereas the perylene core is basically unaffected.

Let us now discuss the density of states projected (PDOS) on the different PTCDA atoms (Figs. 3 and 4 for C and O atoms, respectively) adsorbed on the Al(111) surface. In order to have further insights about the interaction between PTCDA and Al, we show the PDOS for the corresponding atoms relative to isolated PTCDA; the energy reference of the PTCDA levels has been chosen so that the HOMO is 1.5 eV below the Fermi level, as obtained from the calculated band lineup (see below). As expected, the molecular levels

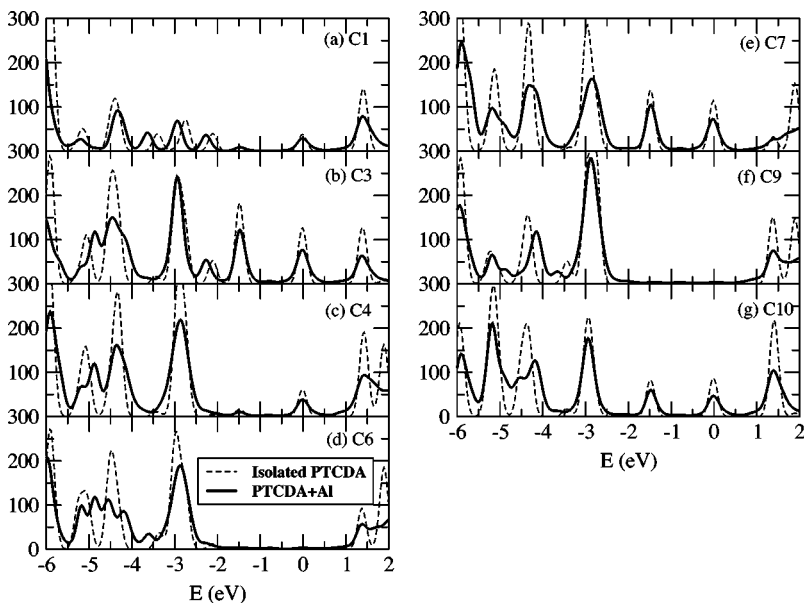


FIG. 3. Projected density of states of different C atoms (see Fig. 1 for atom labels) in the PTCDA/Al junction, with the Fermi level set to zero of the energy scale. The solid (dashed) line denotes the adsorbed (isolated) molecule. A Gaussian smearing of 0.1 eV is used.

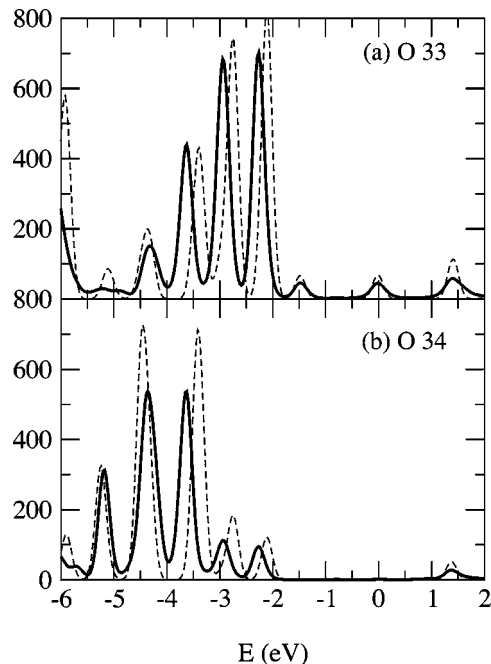


FIG. 4. Projected density of states of different O atoms (see Fig. 1 for atom labels) in the PTCDA/Al junction. The solid (dashed) line denotes the adsorbed (isolated) molecule. A Gaussian smearing of 0.1 eV is used.

are generally broadened by the interactions with the continuum of metallic energy levels. It is clear that, especially in proximity of the Fermi level, most of the levels are unperturbed upon adsorption on Al and that the main result of the interaction is a rigid energy shift, which finally determines the location of the molecular orbitals relative to  $E_F$ . On the other hand, there are new features [such as the peak at around -5 eV in Figs. 3(b)–3(d)] or peaks [see the -4–2-eV energy range in Fig. 4(a)] whose position is shifted with respect to the molecule, reflecting the intramolecular modification of the molecular levels induced by the interaction with the Al substrate.

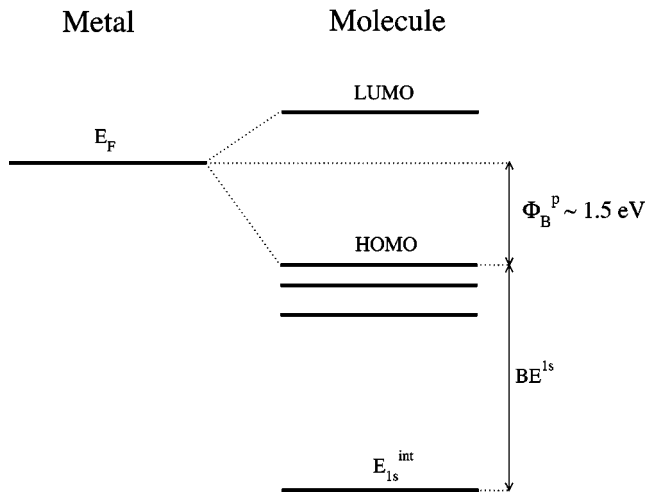


FIG. 5. Schematic diagram of energy levels at PTCDA/Al[111] junction.

### B. Schottky barrier height

In this section, we focus on the potential lineup between the metal and the molecule. Let us first recall that the usual procedure to evaluate the Schottky barrier height (SBH) within all-electron first-principles calculations is based on core levels as reference energies<sup>28,29</sup> and is obtained as the sum of an interface and bulk contributions (see Ref. 30 for details). Following a similar approach in the case of the metal/molecule interface, as shown in Fig. 5, we obtain the SBH as  $\Phi_B^p = E_F - E_{1s}^{int} + BE^{1s}$ . In this way, we explicitly take into account the charge rearrangement at the interface (which determines the relative position of  $E_F$  with respect to the  $1s$  core level energy of the C6 atom in the PTCDA/Al system, denoted as  $E_{1s}^{int}$ ) and a bulk contribution (given by the binding energy of the same core level within the isolated molecule, denoted as  $BE^{1s}$ ). The bulk contribution of the Al side is *built in*, since it is expected that the Fermi level of the interface coincides with the Fermi level of a single Al slab (i.e., no PTCDA adsorbed). Quasiparticle corrections are not included in the present calculation.

In our case, the calculated SBH is  $\Phi_B^p \sim 1.5$  eV. Note that the different sources of numerical errors (such as the choice of different C atoms within the molecule, different choice of the core levels, finite size of the slab, etc.) lead to an uncertainty on  $\Phi_B^p$  of about 0.2 eV. The  $n$ -type SBH (i.e., the difference between the PTCDA LUMO and  $E_F$ ) can be obtained as  $\Phi_B^n = E_{gap}^{PTCDA} - \Phi_B^p$ , i.e., as the difference between the PTCDA band gap,  $E_{gap}$  and the  $p$ -type SBH,  $\Phi_B^p$ . However, due to well known failures of DFT in correctly describing the excited states, the band gap is strongly underestimated (i.e., our calculated value is  $E_{gap}^{DFT} \sim 1.4$ – $1.5$  eV, whereas the experimental value of the optical band gap is  $E_{gap}^{exp} = 2.2$  eV).<sup>8</sup> Therefore we use the experimental value for the band gap and we obtain  $\Phi_B^n = 0.7$  eV. Note that the position of the calculated LUMO with respect to  $E_F$  (shown in Fig. 3 as basically coincident) is an artifact of the calculation, due to the above-mentioned errors within DFT in treating excited states. In this respect, we point out that the possibility that the incorrect LUMO energy position results in a dif-

ferent charge rearrangement at the interface — and therefore in a different SBH value — cannot be ruled out. However, it is not likely that the character of the contact will be changed, the PTCDA/Al junction still showing a rectifying behavior. Moreover, our calculated SBH value is basically unaffected by the PTCDA height with respect to the Al substrate, previously denoted as  $d$  (deviations of  $\Phi_B^p$  by less than 0.05 eV are obtained for changes in  $d$  of about 5%).

As for the comparison between theory and experiments, we point out that, to our knowledge, PTCDA/Al interfaces grown by depositing molecules on the metal substrate have not been studied yet. PTCDA/Al junctions obtained in the opposite deposition sequence and exposed in air lead to a blocking contact.<sup>31</sup> Experiments performed for PTCDA films deposited on different metals<sup>13</sup> (i.e., Mg, Sn, In, Au) resulted in a strong “pinning” of the Fermi level about 2 eV above the highest occupied molecular orbital (HOMO), irrespective of the deposited metal. This would suggest that the deposition of PTCDA films on an Al surface would also lead to a SBH of the order of 2 eV. Our value is smaller (by a few tenths of eV) than this inferred value, although the character of the contact is qualitatively the same. The reason of this slight disagreement could be ascribed to (i) differences in the interface geometry and (ii) DFT approach. Finally, it was experimentally shown that strong interface dipoles exist at PTCDA/metal junctions, invalidating the Schottky-Mott limit.<sup>8</sup> Our results are perfectly consistent with this picture: the Schottky-Mott value in the case of PTCDA/Al would be  $\Phi_B^p = 2.35$  eV, clearly larger than our calculated value.

### V. PTCDA/AG: RESULTS AND DISCUSSION

As for the PTCDA/Ag junction, the technical and structural details (such as number of metallic layers and of atoms, PTCDA flat-lying geometry, etc.) are the same as in the Al case, except for the metal lattice constant used ( $a_{Ag} = 4.09$  Å).<sup>24</sup> In the case of the Ag surface, our calculations do not predict a bound configuration for the PTCDA/Ag system, i.e., the total energy vs distance between the PTCDA molecule and the Ag surface (not reported) does not show a minimum (at variance with the Al case—see inset in Fig. 2), but rather shows a monotonically decreasing trend, eventually asymptotically leading to the sum of the isolated-PTCDA and the Ag-surface constituents. The lack of an equilibrium bound configuration can be ascribed to the use of the PBE approximation, often suggested as an exchange-correlation functional that leads to “underbinding.” In order to further investigate this aspect, we performed calculations using the LDA, by rigidly moving the PTCDA molecule along the  $z$  direction, keeping the  $x$  and  $y$  atomic coordinates fixed: a bound configuration could be found, giving a minimum distance between the organic molecule and the metallic substrate at about 2.8 Å, in quite good agreement with the experimental value ( $d \sim 3$  Å).<sup>32</sup> These results suggest that, irrespective of the different functional (local-density approximation vs GGA, or different GGA flavors), the adsorption mechanism between PTCDA and Ag can be definitely identified as physisorption, the interaction being even weaker than with the Al surface. This is consistent with the expected

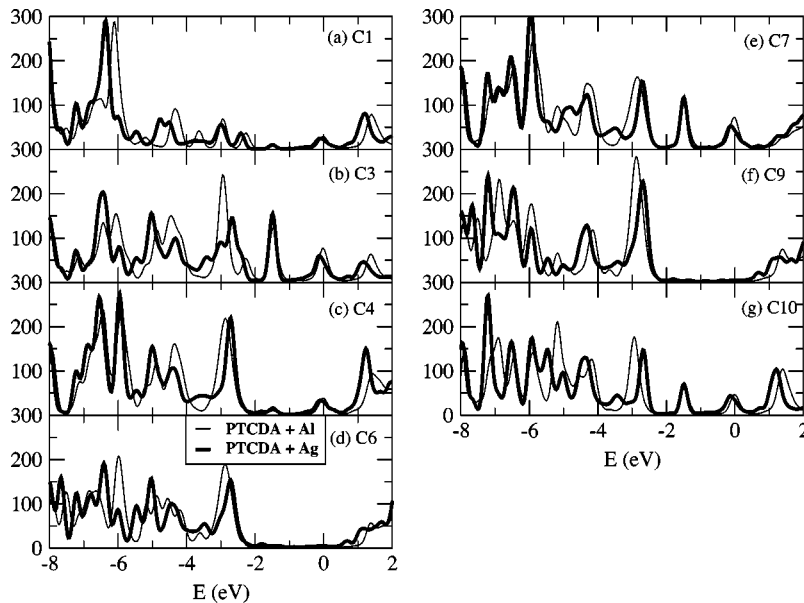


FIG. 6. Comparison between the projected density of states of different C atoms (see Fig. 1 for atom labels) in the PTCDA/ $X$  ( $X$ =Al, Ag) junction, with the Fermi level taken as zero of the energy scale. The bold (thin) solid line denotes the PTCDA/Ag (PTCDA/Al) junctions. A Gaussian smearing of 0.1 eV is used.

lower reactivity of the noble metal, Ag, compared to the free-electron-like metal, Al. Due to the lack of an equilibrium configuration within GGA, from here on, we will discuss the PBE results obtained for a PTCDA/Ag interface, where the distance between the organic molecule and the metallic substrate is set to the experimental value ( $d \sim 3$  Å).<sup>33</sup>

As for charge-transfer issues, we point out that the Mulliken charges show very similar values to the PTCDA/Al case: the metallic surface is positive, whereas the PTCDA molecule gains electrons from the underlying substrate.

Let us now come to the most interesting issue, i.e., the potential line-up. In Fig. 6 we show the PDOS of C atoms in the PTCDA/Ag system (bold solid line), compared with the PTCDA/Al case (thin solid line). As pointed out for Al, the interactions between molecular states and metallic levels broaden the  $\delta$ -like features of the isolated PTCDA molecule. In particular, small differences with respect to the PTCDA/Al case appear (see energy regions around  $-3$  eV), giving rise to new features. However, in the interesting energy range, i.e., in proximity of the Fermi level, the situation is very similar: the PTCDA HOMO is pinned at about  $-1.5$  eV below  $E_F$ , exactly superimposed to the PTCDA HOMO in the Al case, therefore resulting in the same SBH. We remark that this same value of  $\Phi_B^p$  is obtained for different distances of PTCDA from the Ag surface; therefore the lack of a correct description in the equilibrium distance within the GGA-PBE approximation does not result in any related errors regarding the potential lineups. In summary, our results show that (i) the Fermi level is pinned at the same energy position, irrespective of details in the interface geometry and of the underlying metal (Al or Ag), in agreement with experimental results,<sup>13</sup> and (ii) DFT, despite errors arising from the incorrect treatment of excited states, seems able to correctly describe the trend of  $\Phi_B^p$  as a function of the

metal in organic/metal junctions, even though the absolute value of the Schottky barrier height might be affected by some errors (of the order of a few tenths of eV).

## VI. CONCLUSIONS

*Ab initio* calculations have been performed for PTCDA/Al(111) and PTCDA/Ag(111) junctions, using the DMol<sup>3</sup> code within the density-functional theory. In the Al case, the small binding energy and the quite large interplanar distance between organic overlayer and metallic substrate suggests that the interaction is rather weak. In the Ag case, the interaction is even weaker than with Al, as expected for the less reactive noble metal. In both Al and Ag cases, the analysis of Mulliken population resulting from the self-consistent DFT charge rearrangement leads to a charge transfer of about 0.9 electrons, therefore leading to a positively charged metallic surface and to a negatively charged PTCDA; moreover, we find that the main modifications with respect to the isolated PTCDA molecule occur in the anhydride molecular end groups. The technologically important problem of the organic/metal contact is addressed by means of first-principles calculations taking into account both the charge rearrangement at the interface and bulk contributions of the separate constituents. Within our DFT approximation, the calculated value of the Schottky barrier height is about 1.5 eV for both Al and Ag, leading to a blocking contact. Our results show that the position of Fermi level with respect to the HOMO is the same for different underlying metals, in agreement with experimental findings.

## ACKNOWLEDGMENTS

We acknowledge the EU project “DIODE” (Contract No. HPRN-CT-1999-00164) and support from CINECA-Iniziativa Trasversale Calcolo Parallelo through INFN.

- <sup>1</sup>H.E. Katz, *J. Mater. Chem.* **7**, 369 (1997).
- <sup>2</sup>W. Brütting, S. Berleb, and A.G. Mückl, *Org. Electron.* **2**, 1 (2001); S.R. Forrest, *Chem. Rev. (Washington, D.C.)* **97**, 1793 (1997).
- <sup>3</sup>D. Lamoen, P. Ballone, and M. Parrinello, *Phys. Rev. B* **54**, 5097 (1996).
- <sup>4</sup>A. Palma, A. Pasquarello, and R. Car, *Phys. Rev. B* **65**, 155314 (2002).
- <sup>5</sup>R.Q. Zhang, W.C. Lu, C.S. Lee, L.S. Hung, and S.T. Lee, *J. Chem. Phys.* **116**, 8827 (2002).
- <sup>6</sup>R.I.R. Blyth, F. Mittendorfer, J. Hafner, S.A. Sardar, R. Duschek, F.P. Netzer, and M.G. Ramsey, *J. Chem. Phys.* **114**, 935 (2001).
- <sup>7</sup>Y. Xue, S. Datta, and M.A. Ratner, *J. Chem. Phys.* **115**, 4292 (2001).
- <sup>8</sup>A. Hirose, A. Kahn, V. Aristov, P. Soukiassian, V. Bulovic, and S.R. Forrest, *Phys. Rev. B* **54**, 13748 (1996).
- <sup>9</sup>K. Glöckler, C. Seidel, A. Soukopp, M. Sokolowski, E. Umbach, M. Böhringer, R. Berndt, and W.D. Schneider, *Surf. Sci.* **405**, 1 (1998).
- <sup>10</sup>T. Schmitz-Hübsch, T. Fritz, R. Staub, A. Back, N.R. Armstrong, and K. Leo, *Surf. Sci.* **437**, 163 (1999).
- <sup>11</sup>M. Böhringer, W.D. Schneider, K. Glöcker, E. Umbach, and R. Berndt, *Surf. Sci.* **419**, L95 (1998).
- <sup>12</sup>F.S. Tautz, M. Eremtchenko, J.A. Schaefer, M. Sokolowski, V. Shklover, K. Glöcker, and E. Umbach, *Surf. Sci.* **502-503**, 176 (2002).
- <sup>13</sup>I.G. Hill, D. Milliron, J. Schwartz, and A. Kahn, *Appl. Surf. Sci.* **166**, 354 (2000).
- <sup>14</sup>J.P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- <sup>15</sup>J.P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13 244 (1992).
- <sup>16</sup>B. Delley, *J. Chem. Phys.* **92**, 508 (1990).
- <sup>17</sup>B. Delley, *J. Chem. Phys.* **113**, 7756 (2000).
- <sup>18</sup>H.J. Monkhorst and J.D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- <sup>19</sup>B. Delley, *Int. J. Quantum Chem.* **69**, 423 (1998).
- <sup>20</sup>W.T. Geng, Y.-J. Zhao, A.J. Freeman, and B. Delley, *Phys. Rev. B* **63**, 060101 (2001).
- <sup>21</sup>See, for example, S. Picozzi, Y.-J. Zhao, A.J. Freeman, and B. Delley, *Phys. Rev. B* **66**, 205206 (2002), and references therein.
- <sup>22</sup>D. Porezag, Th. Frauenheim, Th. Khler, G. Seifert, and R. Kaschner, *Phys. Rev. B* **51**, 12 947 (1995).
- <sup>23</sup>M. Elstner, D. Prezag, G. Jugnickel, J. Elsner, M. Haugk, Th. Frauenheim, S. Suhai, and G. Seifert, *Phys. Rev. B* **58**, 7260 (1998).
- <sup>24</sup>*Solid State Physics*, edited by N. W. Ashcroft and N. D. Mermin (Saunders College, Philadelphia, 1976).
- <sup>25</sup>See Ref. 16 in A. Palma, A. Pasquarello, and R. Car, *Phys. Rev. B* **65**, 155314 (2002).
- <sup>26</sup>J.M. Pacheco and J.P. Prates Ramalho, *Phys. Rev. Lett.* **79**, 3873 (1997), and references therein.
- <sup>27</sup>R.S. Mulliken, *J. Chem. Phys.* **23**, 1833 (1955); D. Sanchez-Portal, E. Artacho, and J.M. Soler, *J. Phys.: Condens. Matter* **8**, 3859 (1996).
- <sup>28</sup>S.H. Wei and A. Zunger, *Phys. Rev. Lett.* **59**, 144 (1987).
- <sup>29</sup>S. Massidda, B.I. Min, and A.J. Freeman, *Phys. Rev. B* **35**, 9871 (1987).
- <sup>30</sup>S. Picozzi, A. Continenza, S. Massidda, and A.J. Freeman, *Phys. Rev. B* **57**, 4849 (1998); S. Picozzi, A. Continenza, G. Satta, S. Massidda, and A.J. Freeman, *ibid.* **61**, 16 736 (2000).
- <sup>31</sup>S.R. Forrest, M.L. Kaplan, P.H. Schmidt, W.L. Feldmann, and E. Yanowski, *J. Appl. Phys.* **41**, 90 (1982).
- <sup>32</sup>B. Krause, A.C. Durr, K.A. Ritley, F. Schreiber, H. Dosch, and D. Smilgies, *Appl. Surf. Sci.* **175-176**, 332 (2001).
- <sup>33</sup>The effects of the LDA on the electronic properties will be published elsewhere.