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Organic molecular crystals in electric fields

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Abstract

We present ab initio density functional (DFT) calculations of the electronic properties of organic molecular crystals surfaces in an electric field. We investigate the electronic structure of small slabs of benzene (six layers) and anthracene (four layers) and study their changes due to electric fields perpendicular to the slab surfaces. For extreme fields, charge transfer between the two surfaces could occur in the simulation. We found that benzene and anthracene show a different behavior due to the different electron affinity. While in anthracene two charged layers form at the two surfaces, one of electron type and the other of hole type, electrons from benzene slab are pulled out to vacuum due to negligible or negative electron affinity.

Keywords: Density functional calculations; Aromatics; Field effect; Surface electronic phenomena (work function, surface potential, surface states, etc.)

1. Introduction

Organic molecular crystals (OMC) attracted considerable interest over the last decade. These materials have been successfully used as semiconducting layers for field effect transistors (FET) [1], so they have the potential to be used as alternative materials to semiconductors in electronic devices. Their advantages are the low cost, the excellent mechanical properties, and the possibility to modify their properties with organic chemistry techniques. They are ideal candidates for electronic devices on flexible substrates. However, until now, extensive use in electronic industry has been hindered by their low electron mobilities. Improving the fabrication technology and the properties of these materials and investigating different operating conditions are current trends in research.

Recently, there has been significant progress in purification and mono-crystal growth technology and the reported parameters for field-effect transistors with organic molecular crystal substrates are comparable with devices based on amorphous silicon [1,2]. In this work we present the band structure of two molecular crystals, namely benzene and anthracene, and study the changes of the electronic structure induced by an external electric field. In

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particular, we explore the possibility to dope the surfaces with a sufficiently strong electric field.

For the modeling of the electronic properties of these organic molecular crystals, we use density functional theory (DFT). The reliable predictions of this theory have been tested countless times in covalent and metallic systems. However, even the most sophisticated approximations of DFT, when applied to molecular crystals, show their intrinsic limitations. In these materials there are two quite distinct chemical bonds: strong covalent bonds within a single molecule and weak molecule–molecule bonds responsible for the cohesion of the molecular solids [13]. Within DFT, in the local density approximation (LDA) or in the generalized gradient approximation (GGA), one cannot account for the van der Waals forces which are an important part of the molecule–molecule interaction. However once the crystal geometry is chosen reasonably, the DFT description is quite reasonable even for molecular crystals. In this paper we focus on the response of slabs of benzene and anthracene to external electric fields, calculated at the GGA level, borrowing from experiment the geometrical structure [11] and keeping it fixed in an electric field.

We consider two slabs. One is made of six benzene layers and the other of four anthracene layers. Increasing the intensity of the electric field, the slabs first polarize with an induced surface charge proportional to the field. Successively, since the bandwidth of these materials is much smaller than the gap, and our slabs are very thin, we can observe the Wannier–Stark localization of the electronic states taking place in each layer with a field smaller than the one required to close the gap. Finally, with very large fields, the gap between the positive and the negative face closes. The closing of the gap corresponds to charge transfer. According to the method of Kunc and Resta [3,4], we use a saw-shaped potential to simulate the electric field. This potential is compatible with periodic boundary conditions and has its minimum in the center of the vacuum region. The value of the potential at the minimum depends on the field intensity and on the supercell length. If the vacuum width is sufficiently large, electrons are always transferred to vacuum. However, reducing the amount of vacuum, it is possible to control the minimum value of the potential in vacuum, and in principle to induce charge transfer between the two surfaces. In practice, we found that in benzene electrons are always transferred to vacuum signaling negative electron affinity. Only in anthracene localized surface charges could be produced in strong fields.

2. Computational details

All calculations were carried out within the GGA approximation and with the expression for the exchange and correlation energy introduced by Perdew, Burke and Ernzerhof (PBE) [5]. The ultrasoft pseudo-potentials [6,7] of hydrogen and carbon have parameters as described in Ref. [10]. Plane waves up to an energy cutoff of 30 Ry for the wavefunctions and 180 Ry for the charge density, were used. The benzene slab has six molecular layers with two molecules per layer. We choose a (0 1 0) surface (see Fig. 1). For this orientation every mono-molecular layer has two molecules in the surface unit cell. The position of the molecules is taken as in truncated benzene bulk. In Fig. 1 we show the benzene slab seen from the (0 0 1) direction. The super-cell edges are $a = 7.29$ Å, $b = 36.46$ Å, and $c = 6.74$ Å. The (1 0 0) surface of anthracene is modeled by four layers slab (see Fig. 1). This surface allow us to have only one molecule per layer in the surface unit cell. The position of the molecules is taken as in truncated anthracene bulk [11]. In Fig. 1 we show the anthracene slab seen from the direction (0 1 0). The supercell has monoclinic symmetry. The lengths of the supercell edges are $a = 23.28$ Å, $b = 6.04$ Å, and $c = 11.19$ Å. The angle between vectors $\vec{a}$ and $\vec{c}$ is 124.7. The applied field is perpendicular to the surface in the direction $\vec{b} \times \vec{c}$. A 3×3 Monkhorst and Pack mesh [8] of k-points has been used to sample the 2D Brillouin zone (BZ) for both supercells. When the gap closes in large field we need to introduce a Fermi level and treat the slabs as metals. For that we use the Methfessel–Paxton [9] method with a smearing parameter $\eta = 27$ meV. A vacuum space corresponding to approximately two missing mono-molecular layers (of width 8.26 Å for benzene and 4.87 Å for anthracene) separates the periodically repeated slabs.

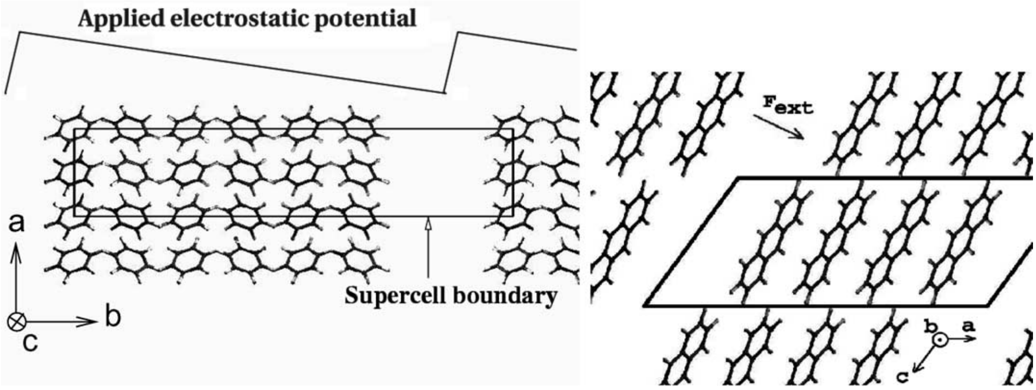

Fig. 1. Geometry of (left panel) the six layer benzene slab and (right panel) of the four layer anthracene slab. The unit cell and the applied saw-tooth potential are indicated.

In order to study the effect of an electric field on benzene and anthracene surfaces, we have applied an external electric field via the method proposed by Kunc and Resta [3,4]. In this method, a saw-like potential is added to the bare ionic potential. We show in Fig. 1 the shape of the saw-tooth shaped external potential added in the simulation of benzene and anthracene slabs. Actually, the field induces a dipole in the slabs and one should correct for the electric field induced by the periodic boundary conditions as described for instance in Ref. [16]. In this work however, we are interested in the qualitative effects of the field and, in this paper, we present results obtained without correcting for this spurious electric field. We have considered two different fields $E = 3 \times 10^{-3}$ a.u. (3.5×10^{-3} a.u.) and $E = 5 \times 10^{-3}$ a.u. ($= 1.4 \times 10^{-2}$ a.u.) for benzene (anthracene). Note that 1×10^{-3} a.u. $= 5.15 \times 10^{6}$ V/cm. These fields have been chosen because the first is sufficient to produce a Wannier–Stark localization of the levels on each molecular layer, while the second induces the gap closing.

3. Results and discussion

In Fig. 2 we show the band structure of the benzene (anthracene) slab at zero electric field and for the two fields $E = 3 \times 10^{-3}$ a.u. and $E = 5\times 10^{-3}$ a.u. ($E = 3.5 \times 10^{-3}$ a.u. and $E = 1.4 \times 10^{-2}$ a.u.). We show only the energy window between -2.5 and 5.5 eV (-2.0 and 3.5 eV) around the top of the valence band. In this energy window the HOMO-1, the HOMO and the LUMO derived bands are visible. The zero of the energy is taken at the top of the valence band. The path in the two dimensional BZ is shown in the inset of the figure.

The band structure of the molecular crystals in zero electric field shows a small dispersion which reflects the weak chemical interactions of benzene and anthracene molecules among themselves. The bandwidth of the HOMO and LUMO derived bands are 0.73 and 0.70 eV respectively for the benzene slab and 0.3 and 0.4 eV for the anthracene slab. The band gap in benzene is $E_g = 4.4$ eV while it is $E_g = 2.1$ eV in anthracene. Our band gap of anthracene is in agreement with previous GGA calculation [12], however it is known that GGA underestimates band gap. Actually experimental value of the band gap in anthracene is 3.9 eV according Ref. [14]. The band gap between HOMO-1 and HOMO bands in benzene is $E'_g = 1.2$ eV and $E'_g = 0.9$ eV in anthracene. In the benzene slab, we have 12 molecules and the HOMO and the LUMO derived bands are formed by 24 bands each, since both the HOMO and the LUMO of the benzene molecule are twofold degenerate. In the anthracene slab, with four molecules, the HOMO and LUMO derived bands are formed by 4 bands since both the HOMO and the LUMO are non-degenerate.

The distance between different layers in benzene (anthracene) is $d = 4.7$ Å ($d = 2.4$ Å). By applying

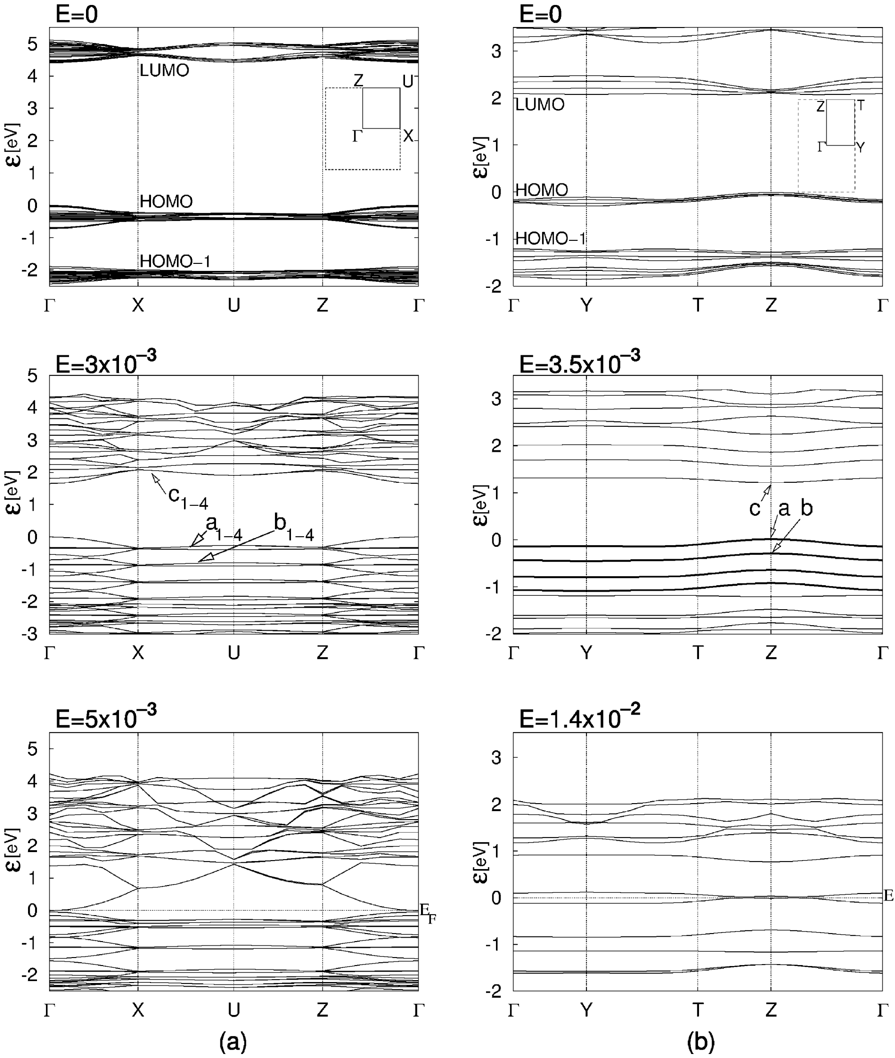

Fig. 2. Electronic structure of the benzene (a) and anthracene (b) slabs in increasing fields. The cases of zero (1), medium ($E = 3 \times 10^{-3}$ (3.5×10^{-3}) a.u.) (2), and band closing ($E = 5 \times 10^{-3}$ (1.4×10^{-2}) a.u.) (3) fields are presented. The surface BZ and the high symmetry points are indicated in the insets. Note a clear Wannier–Stark localization as suggested by HOMO ladders already for middle fields.

a field of 3×10^{-3} a.u. (3.5×10^{-3} a.u.) the bands split due to the different position of the molecular layers in the potential due to the electric field. Field induced shift of molecular levels gets out of levels resonance and localization may arise. In fact at this field intensity the electronic orbitals are localized in each molecular layer as we illustrate in Fig. 3 where the planar average of a few HOMO and LUMO derived states is shown. In benzene, the application of the field splits the HOMO derived bands into six groups of four bands. These four bands correspond to the four HOMO derived states of the two benzene molecules per layer. The highest HOMO derived energy bands (a in the figure) are localized on the right surface, while the lowest LUMO derived energy bands (c in the figure) are localized on the left surface. Anthracene has only one molecule per mono-molecular layer and all states are non-degenerate, thus the HOMO-derived bands split into four single bands. The bandwidths of the HOMO and LUMO derived bands which are due to the intra-layer

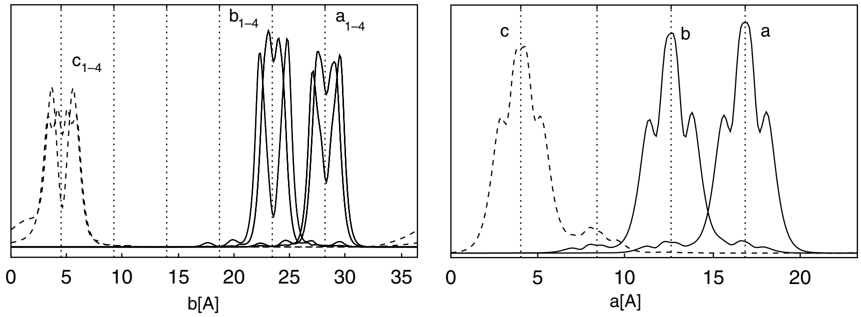

Fig. 3. The planar average of the square modulus of the Kohn–Sham orbitals at the Γ (a) and Z (b) points of the benzene and anthracene BZ illustrate the localization of the states. The centers of the molecular layers are indicated by vertical lines. The labels of the states correspond to the labels in Fig. 2.

molecule–molecule interactions, are all similar and similar to the bandwidth of the HOMO derived level in zero field indicating a small contribution of the molecular Stark shift to the overall shape of these bands at these electric fields.

For external field $E = 3 \times 10^{-3}$ a.u. in benzene ($E = 3.5 \times 10^{-3}$ a.u. in anthracene), the splitting of molecular derived bands as seen in Fig. 2 is about 0.4 eV (0.2 eV in anthracene). The expected splitting would be eEd/ϵ 0.16 eV (0.06 eV), where experimental values of the dielectric constant $\epsilon = 2.3$ [15] (3.55) [14] were used. Large part of this discrepancy can be attributed to the spurious electric field introduced by periodic boundary conditions [16,20]. Assuming a linear behavior of the splittings of the HOMO and LUMO derived bands, we estimate the closing of the band gap with a field $eE = E_g\epsilon_{\text{eff}}/L$, where L is the thickness of the slab, estimated as the distance of the molecular centers on the opposite surfaces. With $L = 23.7$ Å ($L = 7.3$ Å) for benzene (anthracene) we get the estimate of the field $E_{\text{crit}} \approx 5 \times 10^{-3}$ a.u. ($E_{\text{crit}} \approx 8 \times 10^{-3}$ a.u. for anthracene) required to close the gap in our slabs. The HOMO-1 states show a similar behavior and since band gaps between HOMO and HOMO-1 bands are smaller $E'_g = 1.2$ eV (0.9 eV) we can expect the HOMO HOMO-1 gap to close in fields 1.3×10^{-3} a.u. (3.6×10^{-3} a.u.). So in Fig. 2, the HOMO HOMO-1 gap is already closed in benzene and near closure in anthracene.

Finally we show in Fig. 2 the electronic bands of benzene (anthracene) with a field 5×10^{-3} a.u. (1.4×10^{-2} a.u.). With these field intensities the band gap is closing in the benzene slab and it is already closed in the anthracene. The benzene and anthracene, at this field intensities, behave in a very different way. In anthracene a LUMO derived state corresponding to a state localized on the left surface (see Fig. 3), closes the gap with a HOMO derived state localized on the right surface. At this point, in our simulation we introduce a Fermi level and treat the slab as a metal in order to partially occupy the HOMO and the LUMO derived states. We find therefore degenerate 2D metallic ground state of the system with 2D electron gas on the left surface and 2D hole gas on the right surface. In benzene, a free-electron vacuum state touches, at the Γ points, the HOMO derived state localized on the right surface. By treating the system as a metal and by looking at the charge profile in the benzene slab one can see that this situation corresponds to electron charge extracted in the vacuum. We could not, by reducing the vacuum, find a geometry in which the benzene slab behaves as the anthracene with a 2D metallic electron sheet on the left surface. This can be explained by marginal or negative electron affinity of the benzene slab. This fact is in agreement with experimental observations [17,18] of negative electron affinity of benzene molecules.

4. Conclusions

In this paper we have presented the HOMO and LUMO derived bands of a six layers benzene slab and of four layers anthracene slab and we have studied the change of this band structure due to an external electric field. We have analyzed very large fields of 3×10^{-3} a.u. for benzene and 3.5×10^{-3} a.u. for anthracene. At this field intensities, we have found in both slabs that the electronic states are localized in each molecular layer. Correspondingly, the band structure shows splittings due to the different positions of the layers in the potential of the electric field. Such splittings are much larger than the Stark splittings of the molecular levels. We have also explored the closing of the gap induced by the field, at a field 5×10^{-3} a.u. for benzene and 1.4×10^{-2} a.u. for anthracene. We have found that in the benzene slab a stable charge transfer between the two surfaces does not occur. The electron escapes to vacuum instead of localizing on the surface. On the contrary in anthracene it is possible to construct a state with a transfer of charge between the left and right surfaces.

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References

[1] C.D. Dimitrakopoulos, S. Purushothaman, J. Kymissis, A. Callegari, J.M. Shaw, Science 283 (1999) 822.
[2] A.R. Brown, C.P. Jarrett, D.M. de Leeuw, M. Matters, Synthetic Metals 88 (1997) 37.
[3] K. Kunc, R. Resta, Phys. Rev. Lett. 51 (1983) 686.
[4] R. Resta, K. Kunc, Phys. Rev. B 34 (1986) 7146.
[5] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[6] D. Vanderbilt, Phys. Rev. B 41 (1990) 7892.
[7] A.M. Rape, K.M. Rabe, E. Kaxiras, J.D. Joannopoulos, Phys. Rev. B 41 (1990) 1227.
[8] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188.
[9] M. Methfessel, A.T. Paxton, Phys. Rev. B 40 (1989) 3616.
[10] A. Dal Corso, Phys. Rev. B 64 (2001) 235118.
[11] Wyckoff, Crystal Structures, vol. 6: The Structure of Benzene Derivatives, second ed., Wiley, 1969–1971.
[12] K. Hummer, P. Puschnig, C. Ambrosch-Draxl, Phys. Rev. B 67 (2003) 184105.
[13] E.A. Silinsh, V. Capek, Organic molecular crystals: Interaction, localization and transport phenomena, Am. Inst. Phys., New York, 1994.
[14] E.A. Silinsh, Organic Molecular Crystals: Their Electronic States, Springer-Verlag, Berlin, 1980.
[15] Available from <http://www.asiinstr.com/dc1.html>.
[16] L. Bengtsson, Phys. Rev. B 59 (1999) 12301;
B. Meyer, D. Vanderbilt, Phys. Rev. B 63 (2001) 205426.
[17] J.R. Frazier, L.G. Christophorou, J.G. Carter, H.C. Schweinler, J. Chem. Phys. 69 (1978) 3807.
[18] P.D. Burrow, J.A. Michejda, K.D. Jordan, J. Chem. Phys. 86 (1986) 9.
[19] S. Baroni, A. Dal Corso, S. de Gironcoli, P. Giannozzi, Available from <http://www.pwscf.org>.
[20] J. Tóbik, A. Dal Corso, J. Chem. Phys. 120 (2004) 9934.