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The nature of the observed free-electron-like state in a PTCDA monolayer on Ag(111)

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Abstract. A free-electron-like band has recently been observed in a monolayer of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) molecules on Ag(111) by two-photon photoemission (Schwalb *et al* 2008 *Phys. Rev. Lett.* **101** 146801) and scanning tunneling spectroscopy (Temirov *et al* 2006 *Nature* **444** 350). Using density functional theory calculations, we find that the observed free-electron-like band originates from the Shockley surface state band being dramatically shifted up in energy by the interaction with the adsorbed molecules, while it also acquires a substantial admixture with a molecular band.

Electronic states at the organic molecule–metal interface are of key importance for electronic and opto-electronic applications since they influence electron transport across the interface directly. These interface states are formed from the interaction between highly dispersive states of the metal substrate and weakly dispersive states of the semiconducting organic molecular layers. The molecular states at the interface shift, broaden and become partially populated or depopulated upon interaction with the metal states. The effect of the organic molecular layers on metal surface states such as the Shockley surface (SS) states on noble metal surfaces is less clear and has recently attracted much attention from observations of dispersive interface states in these systems.

In many cases, upon adsorption of organic molecules on gold and copper surfaces [1]–[6], the SS states were observed from scanning tunneling spectroscopy (STS) and angle-resolved photoemission to experience small energy shifts. In some cases, the fate of the SS and the origin of highly dispersive states turned out to be more complex. A dispersive hybrid band

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was identified by STS at the interface between a monolayer of charge-transfer complexes on a gold surface and was shown by density functional theory calculations to arise from a mixing of metal and molecular states [7]. A free-electron-like band was identified by STS in a monolayer of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) molecules on the Ag(111) surface and was attributed to originate from the lowest unoccupied molecular orbital (LUMO) of the PTCDA molecule [8]. This free-electron-like band was recently also identified in two-photon photoemission experiments by Schwalb *et al* [9], who challenged the interpretation proposed by Temirov *et al* [8]. Based on the observed short lifetime of electrons in this band, Schwalb *et al* argued that this band corresponded to an upward shifted SS band by the interaction with the molecular monolayer. Thus there is a need to carry out electronic structure calculations to resolve this outstanding issue about the origin of the observed free-electron-like state.

In this paper, we present density functional theory (DFT) calculations of the electronic structure of the PTCDA monolayer on an Ag(111) surface and show that the origin of the observed free-electron-like state is an SS state that has been shifted up in energy from the interaction with the molecular monolayer. We also find that the observed free-electron state has acquired character from the LUMO + 1 of the adsorbed molecule.

The electronic and geometric structures of the molecular monolayer on the metal surface were determined from periodic DFT calculations using the projector augmented wave method [10], as implemented in the plane-wave-based VASP code [11]. The surface unit cell of the two structurally inequivalent PTCDA molecules adsorbed on an Ag(111) slab is described in detail by Rohlfing *et al* [12]. The vacuum region is about 16.5 Å. The full geometry relaxation of the molecular monolayer and the two outermost layers of the Ag slab was carried out using a four-layer slab with a plane wave cutoff of 400 eV on a $6 \times 4 \times 1$ k-point grid until the forces acting on the ions were smaller in magnitude than 0.02 eV Å^{-1}. In order to have a good description of the Shockley surface band, a 12-layer slab was used in the calculation of the electronic states. This slab was obtained by adding eight layers of Ag atoms at their bulk positions to the bottom of the structurally optimized four-layer slab.

Following the widely used Tersoff–Hamann approximation [13], the differential conductance measured in STS experiments was approximated using the local density of states (LDOS) calculated for the 12-layer slab at the position of the tip apex. The molecular orbital projected density of states (MO-PDOS) was calculated by projecting the wave functions of the full system onto the wave functions of the isolated monolayer kept in the same geometric structure as for the adsorbed monolayer. The wave-vector-resolved LDOS and PDOS were calculated along a line from the Γ point to the surface Brillouin zone (SBZ) boundary.

Supported by the findings of Rohlfing *et al* [12, 14], we used the local density approximation (LDA) for the exchange-correlation functional. The generalized-gradient approximation (GGA) was found to give too large a bonding distance for the perylene core of about 3.5 Å and too weak a bonding of less than 0.1 eV per molecule. A recent study by Romaner *et al* [15] showed that the inclusion of non-local interactions using a recently developed van der Waals functional [16] in the DFT calculations increased the adsorption energy per molecule to a more realistic value of about 2 eV, but gave also a very large bonding distance of about 3.5 Å. In contrast the LDA was found to give a bonding geometry in much better agreement with standing x-ray diffraction data [17, 18]. The adsorption height of 2.8 Å and the adsorption energy of 2.6 eV per molecule obtained in the LDA were shown to be in good agreement with the corresponding results of 3.1 Å and 2.4 eV for the adsorption height and energy, respectively, obtained from a more fundamental approach to weak adsorption. In this approach, the exact

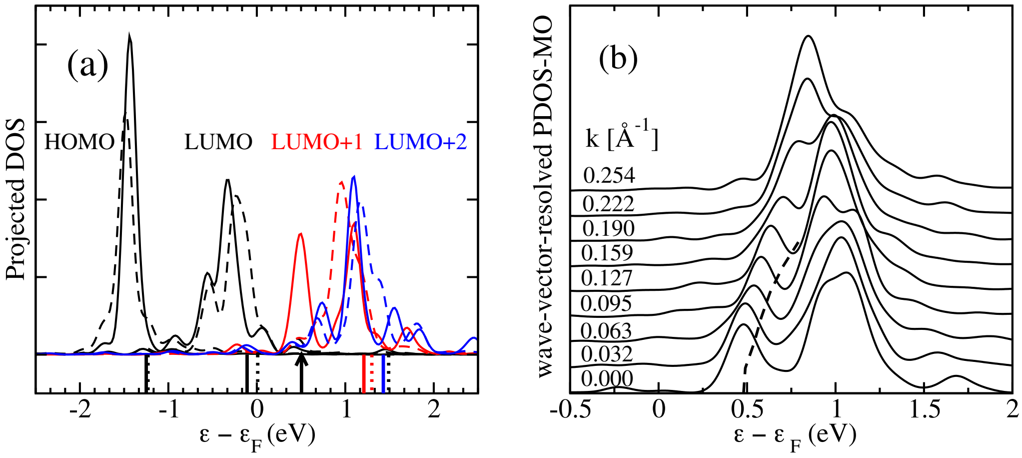

Figure 1. Projected DOS (PDOS) of the adsorbed PTCDA monolayer on the frontier molecular orbitals (MOs) of the isolated PTCDA monolayer. In (a), PDOS on the HOMO, LUMO, LUMO + 1 and LUMO + 2 are taken at the Γ point in the SBZ. The dashed and solid lines correspond to the projected DOS of the two nearly degenerate MOs of the two molecules in the surface unit cell. Their energies when aligning the vacuum levels of the isolated and the adsorbed monolayer are indicated by vertical bars. The vertical arrow indicates the position of the satellite peak in one of the LUMO + 1 states. The dispersion of the projected DOS on the LUMO + 1 is shown in (b) where the dashed line indicates the energies of the peak positions in the PDOS. Both LUMO + 1 states are included in (b).

exchange energy is combined with a random phase approximation for the correlation energy as obtained from the adiabatic connection dissipation fluctuation theorem [14].

Our calculated average height of the perylene cores above the surface is 2.76 Å and the average relative height between the anhydride and carboxylic oxygen atoms is 0.24 Å; both these heights are in good agreement with the corresponding values 2.67 and 0.24 Å obtained by Rohlfing *et al* [12]. They used the SIESTA package, which is based on a localized basis set, and the LDA. However, we find the average height of the anhydride oxygen atoms to be 0.04 Å below the average height of the perylene cores, rather than being 0.08 Å above it, as obtained by Rohlfing *et al* [12].

The character of the electronic states of the adsorbed molecular monolayer on the Ag surface is revealed by the calculated projected DOS on the frontier orbitals of the isolated monolayer, shown in figure 1(a) at the Γ point in the SBZ. For the isolated monolayer, the two inequivalent molecules in the surface unit cell result in two nearly degenerate bands for each highest occupied molecular orbital (HOMO), lowest (LUMO), second lowest (LUMO + 1) and third lowest (LUMO + 2) unoccupied molecular orbitals. The energy splittings are only about 0.1 eV at the Γ point in the SBZ and demonstrate that the direct interactions between the molecules are small. Note that LUMO + 1 and LUMO + 2 are nearly degenerate and their ordering is reversed and hence their labeling is reversed compared to that obtained by Rohlfing *et al* [12].

Upon adsorption, the frontier orbitals shift down in energy and are broadened by the interaction with the metal states. The HOMOs are largely unaffected and shifted down in energy

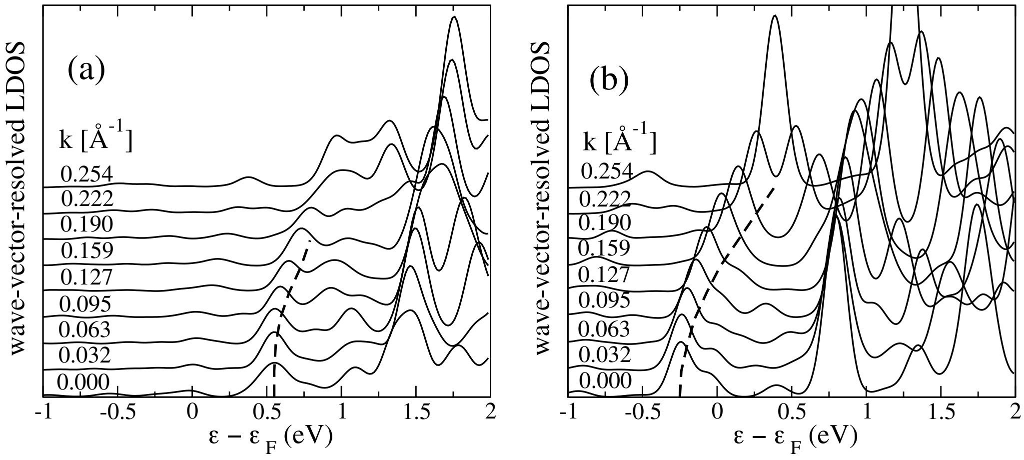

Figure 2. Wave-vector-resolved LDOS of the PTCDA monolayer adsorbed on the Ag slab (a) and the bare side of the Ag slab (b) at a distance of 7 Å from the top Ag layer. The magnitude k of the parallel momentum along the direction in the SBZ boundary is indicated and $k = 0.254\,\text{Å}^{-1}$ corresponds to the zone boundary. The thick dashed lines indicate the energies of the peak positions in the LDOS. The states were broadened by 0.1 eV.

with about 0.41 eV. The two LUMOs broaden and become more or less fully occupied with peak positions −0.32 and −0.21 eV being close to the measured peak positions of the P1 state by STS [8]. This assignment is in agreement with previous studies [12]. Both the LUMO + 1s and LUMO + 2s broaden appreciably and develop satellite structures but remain unoccupied. Of particular note is the pronounced satellite peak at the energy of about 0.5 eV in the PDOS on the LUMO + 1s.

The energy of this satellite peak in the PDOS at the Γ point is close to the onset of about 0.6 and 0.7 eV of the free-electron-like band (P2 state) observed in 2PPE [9] and STS [8], respectively. We note that the energy increases slightly to 0.6 eV when using the GGA for the geometry obtained in the LDA. Furthermore, this peak has a free-electron-like dispersion away from the Γ point, as shown in figure 1(b) by the wave-vector-resolved PDOS on the two LUMO + 1s in the SBZ. The calculated effective mass of $0.5m_e$ is close to the effective mass of about $0.39m_e$ and $0.47m_e$ extracted from the observed FE band in 2PPE [9] and STS [8], respectively. This close agreement between observed and calculated onsets and effective masses suggests that the calculated FE band corresponds to the observed FE band. Note that in this case of relatively delocalized states, the Kohn–Sham states should provide a reasonable zero-order approximation of the one-electron addition spectrum probed by STS. Further support for this assignment in the case of STS comes from a comparison of calculated LDOS with observed STS spectra and images.

As shown in figure 2(a), the FE band identified in the PDOS on the LUMO + 1 also shows up in the wave-vector-resolved LDOS, and this demonstrates that it should be observable in STS. The assignment of the observed FE band to the calculated FE band is further corroborated by the calculated LDOS image at the onset of the FE band corresponding to an energy of 0.50 eV and the Γ point in the SBZ. This image is shown in figure 3(a) and is in good agreement with the observed STS image (inset in figure 3(a) of [8]). At this tip apex–surface distance, this image shows no nodal structure and does not resemble any MO of the PTCDA molecules. However,

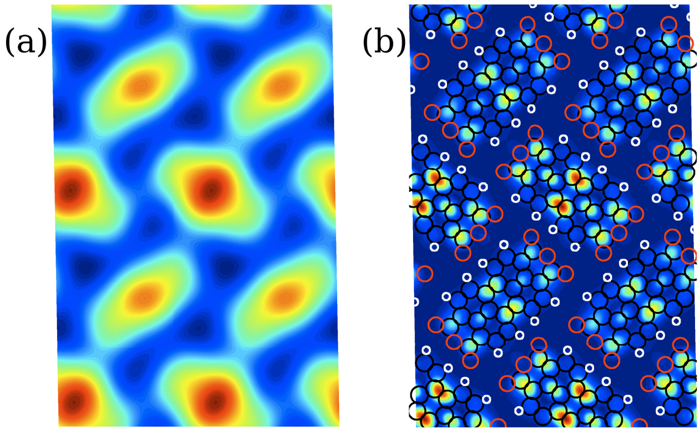

Figure 3. Contour plots of calculated LDOS images of the PTCDA monolayer on Ag(111) for vertical tip–molecule distances of about (a) 7.2 Å and (b) 1.3 Å at an energy of 0.50 eV above the Fermi level and at the Γ point in the SBZ. Red and blue contours correspond to high and low LDOS, respectively. In (b), the H, C and O atoms are represented by white, black and red circles, respectively.

at a much closer distance of about 1.3 Å from the molecular monolayer, the calculated LDOS image in figure 3(b) has a similar nodal structure to the orbital density of the LUMO + 1 state, as expected from the strong overlap of the FE state with the LUMO + 1 state in the PDOS (figure 1(a)). Only LUMO + 1 of the isolated molecule is totally symmetric among the frontier orbitals (see LUMO + 2 in figure 3 of [12]) and can interact with the FE band at the Γ point.

On the bare side of the slab, the SS state band is clearly identified in the wave-vector-resolved LDOS (figure 2(b)). In this calculation, the onset of this SS band is somewhat below the observed value of about −0.06 eV [19] and the calculated effective mass of about $0.36m_e$ is close to the measured value of about $0.40m_e$ [19].

The strong overlap of the FE band with one of the LUMO + 1 (figures 2 and 3) suggests that LUMO + 1 is directly involved in the formation of the FE band as proposed by Temirov *et al* [8]. A direct measure of the overlap is given by the integrated strength of the PDOS over the FE state. This strength is about 0.35 and is a substantial fraction of the total integrated strength of unity of the PDOS of the particular LUMO + 1. Note that the two LUMO + 1 states of the two molecules in the surface unit cell form in-phase and out-of-phase combinations. Only the in-phase combination has an overlap with the free-electron state at the Γ point. The strong overlap of the FE band with the in-phase combination of the LUMO + 1 is further illustrated in the orbital density of this band at the Γ point in the SBZ shown in figure 4. The orbital density decays slowly into the bulk and the density of the π orbitals of the LUMO + 1 state shows up as two peaks on either side of the perylene core.

The alternative proposal by Schwalb *et al* [9] that the FE band originates from the SS band of the bare surface has been investigated by calculating the evolution of the FE band with the vertical height of the molecular monolayer from the surface. In figure 5, we depict the wave-vector-resolved LDOS as a function of a rigid outward shift Δz of the molecular monolayer from its vertical equilibrium distance. The FE band shifts rapidly down in energy with increasing Δz. At $\Delta z = 0.5$ Å, the onset has already shifted down to about 0.1 eV above the Fermi energy and approaches the onset of the SS. Furthermore, the dispersion increases somewhat with increasing

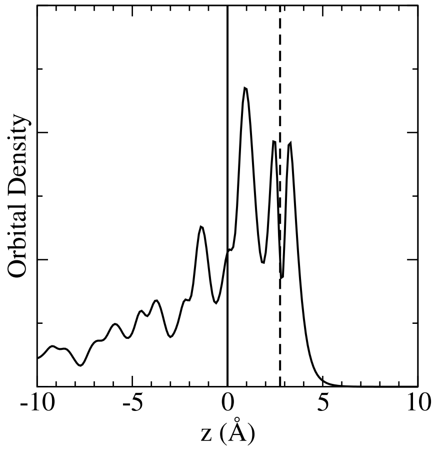

Figure 4. Orbital density of the FE band at the Γ point of the SBZ as a function of the coordinate z perpendicular to the surface. The density has been laterally averaged and the vertical solid line gives the average position of the first layer of Ag atoms. The average position of the perylene core is indicated by the vertical dashed line.

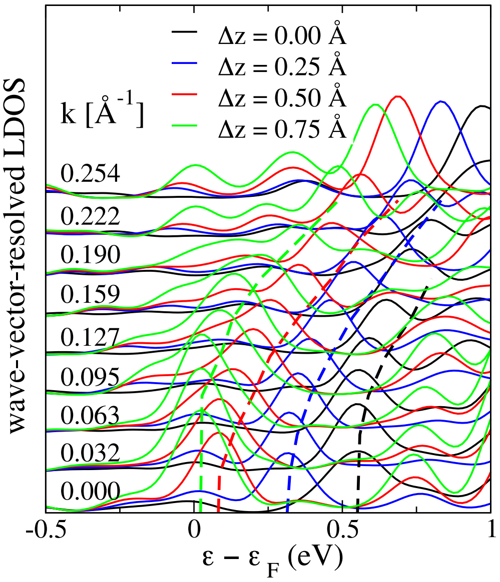

Figure 5. Evolution of wave-vector-resolved LDOS of the PTCDA monolayer adsorbed on the Ag slab with the height Δz of the monolayer from its equilibrium position on the surface. The magnitude k of the parallel momentum along the direction in the SBZ boundary is indicated and $k = 0.254$ Å^{-1} corresponds to the zone boundary. The thick dashed lines indicate the energies of the peak positions in the LDOS. The states were broadened by 0.1 eV.

Δz and becomes closer to the dispersion of the SS band. Thus, the evolution of the FE band with the height of the molecular monolayer shows that the FE band corresponds to an SS band shifted upwards in energy by the interaction of the Ag surface with the adsorbed monolayer and acquiring an admixture with the LUMO + 1.

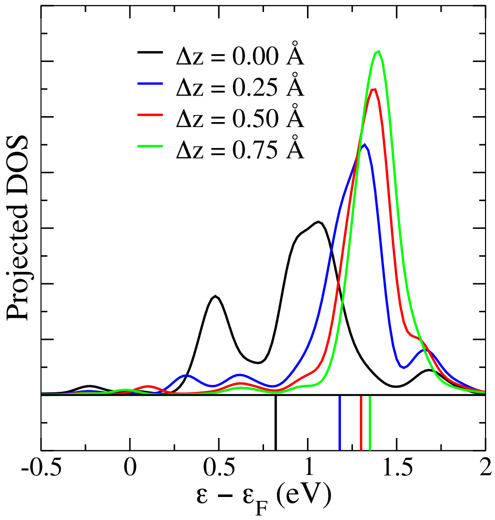

Figure 6. Evolution of the PDOS of the adsorbed PTCDA monolayer on the LUMO + 1 with the height Δz of the monolayer from its equilibrium position on the surface. The projection is taken at the Γ point in the SBZ and both LUMO + 1 states are included. The average energies of the PDOS are indicated by vertical bars. The states were broadened by 0.1 eV.

A more detailed understanding of the interaction of the LUMO + 1 with the SS state is revealed by the behavior shown in figure 6 of the projected DOS on this state at the Γ point of the SBZ as a function of the vertical distance of the monolayer from its equilibrium position. Upon the interaction of the PTCDA monolayer with the Ag surface, the LUMO + 1 broadens and its average energy shifts down in energy with decreasing vertical distance. Only at a very close distance of 0.25 Å does the LUMO + 1 start to develop a significant overlap with the SS at 0.3 eV, which increases dramatically at the equilibrium distance with a concomitant dramatic downward shift of its average energy. Furthermore, this shows that the covalent interaction between the SS band and the LUMO + 1 band does not govern the upward shift of the SS band. Such an interaction alone would give rise to a level repulsion. The upward shift must then be caused by making the one-electron potential more repulsive for the SS band in a similar manner to the mechanism proposed by Schwalb *et al* [9].

In conclusion, we have shown from a density functional theory study that the observed free-electron band in STS and in two-photon photoemission (2PPE) spectroscopy of an adsorbed monolayer of PTCDA molecules on an Ag(111) surface originates from the Shockley surface state being dramatically shifted up in energy by interaction with the adsorbed molecules. The band acquires also a substantial admixture with the LUMO + 1 bands of the molecular monolayer. This finding shows that the metal surface states play an important role in forming dispersive states at the metal–organic interface. Furthermore, upon adsorption of a film of PTCDA molecules, the overlap of the surface band with the LUMO + 1 band in the adlayer has important implications for the level alignment of the valence and conduction bands of the film with respect to the metal states and hence also for the electron transport across the metal–organic interface.

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