Molecular Distortions and Chemical Bonding of a Large π-Conjugated Molecule on a Metal Surface

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Normal incidence x-ray standing wave experiments and density functional theory reveal that 3,4,9,10-perylene-tetracarboxylic-dianhydride chemisorbs on Ag(111) in a *nonplanar* but vertically distorted configuration. The carboxylic O atoms are 0.18 ± 0.03 Å closer to the surface than the perylene core. The distortion is related to weak, local bonds between carboxylic O atoms and the Ag surface which are coupled—through charge transfer into the former lowest unoccupied molecular orbital—to the primary, extended chemisorption bond via the perylene skeleton.

Today, the chemical bonding of small and medium sized molecules to metal surfaces is rather well understood. Prominent examples are CO and benzene, which were studied by experiment and theory on many surfaces [1,2]. Considerable insight has also been gained for aliphatic organic molecules [3]. However, much less is known about the bonding of large π-conjugated molecules to metal surfaces. In particular, structural data concerning adsorption sites and internal atomic coordinates are missing, with very few exceptions [4]. Yet, knowledge of geometric parameters is a prerequisite for any conceptual analysis of relevant bonding mechanisms.

The chemisorptive bonding of large π-conjugated molecules to metal surface is expected to display interesting features. As for small molecules, one anticipates a mutual influence between the surface-molecule bonds and intramolecular bonds [1]. However, due to the larger footprints of these molecules and the presence of functional groups, this interplay can be more multifarious; e.g., it may induce vertical and lateral distortions of the molecule [4]. The here investigated PTCDA (3,4,9,10-perylene-tetracarboxylic-dianhydride [see Fig. 1(a)]) is a prototype of large π-conjugated molecules [5–7]. The planar molecule consists of a perylene core with two anhydride O=C—O—C=O groups attached on opposite sides. We report an experimental and theoretical determination of the vertical bonding distances for the perylene core and the two types of oxygen atoms within PTCDA chemisorbed on the Ag(111) surface. Experimentally we used the normal incidence x-ray standing wave (NIXSW) technique [8]. Our theoretical calculations of the complete adsorption geometry are based on density functional theory (DFT), carried out in the generalized gradient approximation (GGA), employing the SIESTA code [9].

On Ag(111), PTCDA forms a long-range ordered commensurate monolayer with two flat lying molecules per unit cell in a herringbone arrangement [6]. The well-

defined site-specific interaction between PTCDA and Ag(111) [7] makes this system ideally suited for the purposes of the present study. The DFT calculations accurately replicate structural details of the monolayer and yield an adsorption energy of 5.8 eV per molecule. We have verified that the structural relaxation of the three Ag layers used in the calculation yields only negligible deviations from ideal bulk positions (<0.05 Å) and has no significant effect on the PTCDA interface bonding.

From electron spectroscopies [5,7] and the submolecular scanning tunneling contrast [6], some information about the bonding to the Ag(111) surface has already been gathered: the bonding is *chemisorptive*, it occurs mainly on the perylene core of PTCDA, and it involves the formation of a partially filled hybrid orbital, originating from the LUMO (lowest unoccupied molecular orbital) of the free molecule and Ag $5s$ electrons. However, the anhydride groups must be also important, since the bonding of perylene on Ag(111) shows similar features, but is considerably weaker [10].

The NIXSW technique uses that adsorbate atoms located at the positions of the antinode planes of a standing x-rays wave field exhibit a maximum in the photoemission (PE) yield. A variation of the x-ray photon energy around the (111)-Bragg condition shifts the position of the antinodes relative to the substrate lattice planes and thus probes different vertical positions. From a PE yield curve the coherent position d_c and coherent fraction f_c are derived [8]. The former is the averaged vertical distance of the respective photoemitter from the relevant family of bulk lattice planes; the latter describes its actual distribution. For Ag(111) there is no significant surface relaxation ([11] and our DFT results), and d_c values can hence be identified with vertical surface bonding distances. All d_c values quoted in this work also average over the two molecules in the unit cell. The NIXSW experiments have been conducted at the beam line ID32 of the European
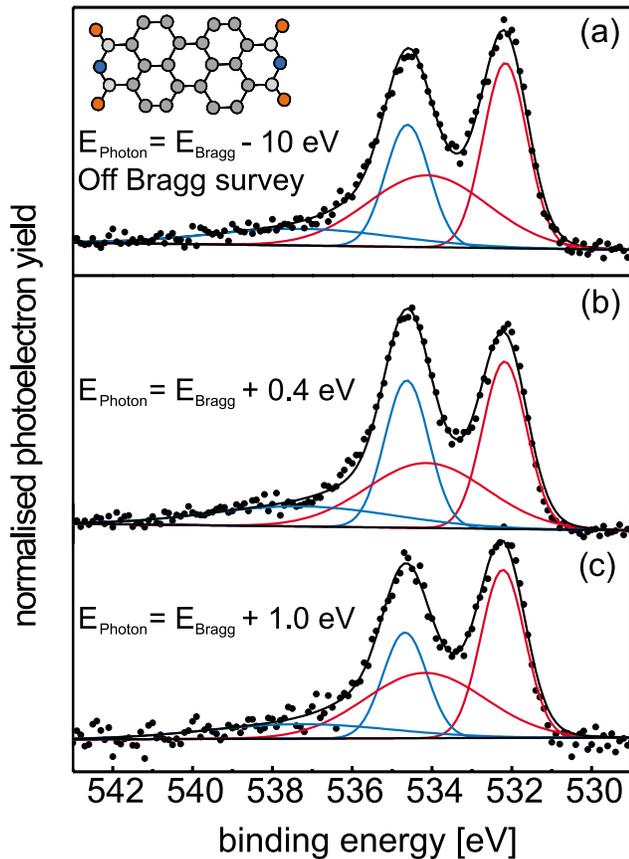
FIG. 1 (color). Photoemission (PE) spectra of the PTCDA O1s level (black dots): (a) at an off-Bragg photon energy, used for determination of peak components (see text); (b),(c) two examples taken at photon energies close to the Bragg energy ($E_{Bragg} = 2633$ eV), used for the NIXSW analysis. Carboxylic (red) and anhydride oxygen (blue) components are both fitted by a doublet. Solid lines: fits to the experimental data. The inset shows the PTCDA molecule. Red/blue circles: carboxylic/anhydride O atoms; light/dark gray circles: C atoms in anhydride groups or perylene core.

Synchrotron Radiation Facility (Grenoble). The preparation of the commensurate PTCDA monolayer was performed as in Ref. [6]. Beam damage of the organic layers was excluded by low energy electron diffraction and x-ray photoelectron spectroscopy.

A set of typical O1s PE spectra is displayed in Fig. 1. Data in the top panel were taken off the Bragg condition. The fitted spectrum is composed of two doublets, one from the carboxylic O atoms, the other from the anhydride O atoms, plus a linear background. Each doublet is composed of a main peak and a broader satellite at higher binding energies [12], which yields a good approximation of the spectral functions of the two O1s core levels within our experimental resolution. At off-Bragg photon energies, i.e., if no standing wave field is present, the areas of the two doublets exhibit a ratio of 2:1, as required by the stoichiometry of PTCDA. The same fitting strategy as in Fig. 1(a) (but with constrained parameters for the relative peak

positions, peak half widths, and relative intensities of the satellites with respect to their main peaks) was used for the evaluation of all PE spectra taken close to the Bragg condition. We find that the relative intensity of the two O1s doublets varies as the photon energy is varied across the Bragg condition [Figs. 1(b) and 1(c)]. This proves that the two types of oxygen atoms within the PTCDA are on a different height above the Ag(111) surface. From fitted spectra as shown in Fig. 1, the total PE yields (areas) of the C atoms and the two chemically nonequivalent O atoms were extracted to obtain PE yield curves, as those displayed in Fig. 2. For the determination of d_c and f_c the curves were fitted using the program "DARE" [13,14]. The f_c values range between 50% and 80%, rendering d_c values meaningful.

Figure 3(a) illustrates the experimentally determined vertical atomic positions. The averaged vertical distance of the C atoms (dominated by the perylene core) is 2.86 ± 0.01 Å, in agreement with Ref. [17]. The four carboxylic O atoms are 0.18 ± 0.03 Å below the plane of the perylene core; the two anhydride O atoms are 0.11 ± 0.06 Å above
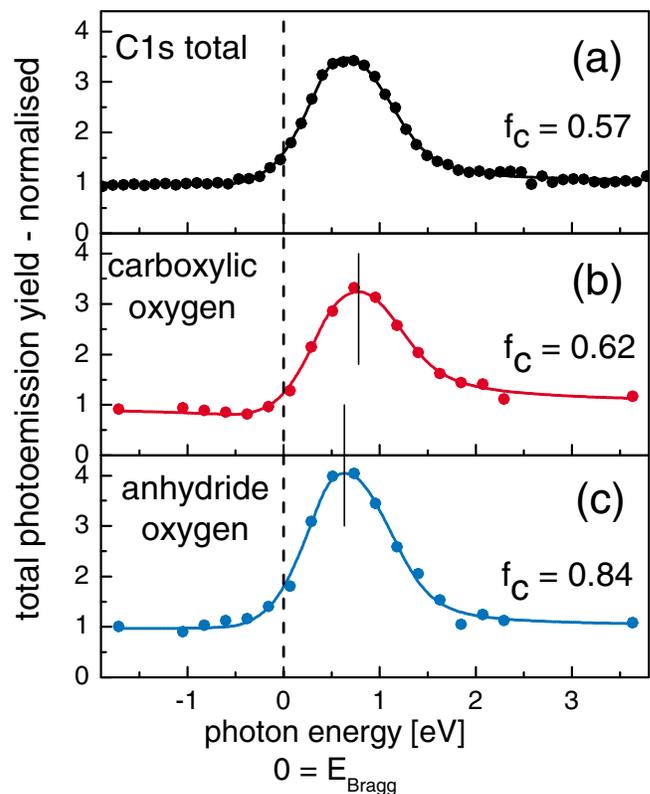

FIG. 2 (color). Total photoemission yield curves as a function of photon energy relative to the Bragg energy (symbols) and fits (solid lines) with respective coherent fractions f_c: (a) carbon, (b) carboxyl oxygen (red), and (c) anhydride oxygen (blue). Data points were taken on a nonequidistant grid for optimized data statistics. The shift in the position of the maximum (indicated for O by vertical lines) and the variation of the background from the left and to the right of the peak are due to different vertical distances of three atom species to the surface.
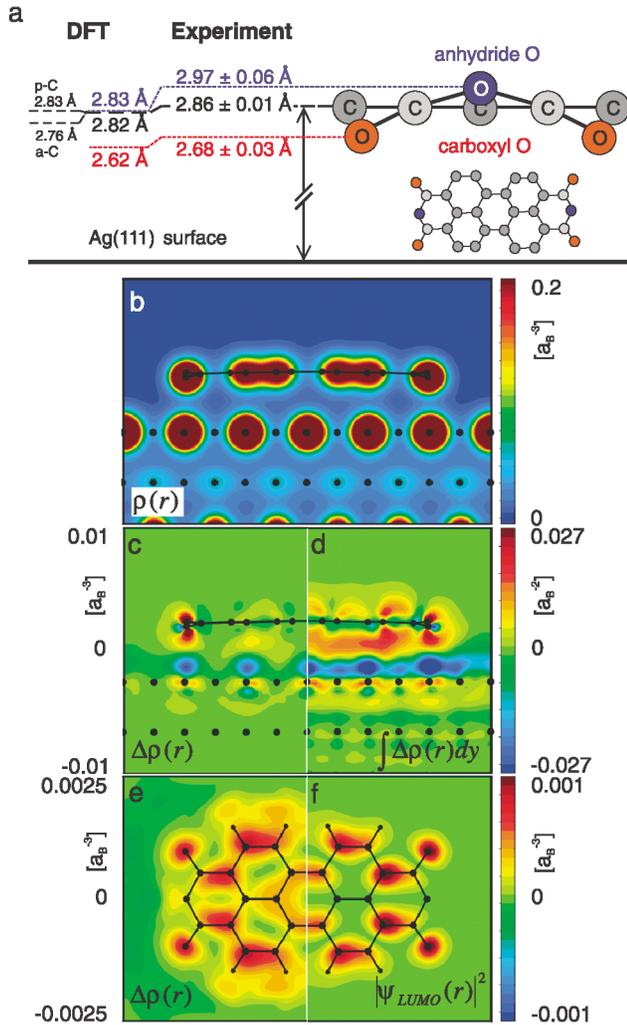
FIG. 3 (color).   (a) Hard sphere model of PTCDA/Ag(111)
with experimentally and theoretically determined vertical dis-
tances. The vertical length scale is expanded by a factor of 3. The
z coordinates on the left refer to the average over C atoms in the
perylene core (p-C) and in the anhydride group (a-C). (b) Total
electron density $\rho(\mathbf{r})$ [18] (vertical cut at the position of car-
boxylic oxygens); color scale ranges from 0 to 0.2 a_B^{-3} ($a_B =$
Bohr radius). Highest charge density in this map corresponds to
1.1 a_B^{-3}. (c)–(e) Difference maps of electron density $\Delta\rho(\mathbf{r})$
(interacting minus noninteracting system): (c) vertical cut as in
(b); (d) summation of vertical cross sections, i.e., $\int \Delta\rho(\mathbf{r})dy$,
integration variable y being along the short axis of molecule.
(e) Horizontal cut 1.3 Å below carbon skeleton of PTCDA.
(f) Horizontal cut as in (e) through probability density of free
LUMO. Note that in (b)–(f) neighboring molecules have been
removed.

it. The vertical distance between the two types of O atoms
is thus 0.29 ± 0.07 Å. Evidently the intrinsically planar
PTCDA molecule is significantly distorted on the Ag(111)
surface, and the four carboxylic O atoms are lowered to the
surface.

   This result is confirmed by DFT calculations [Fig. 3(a)].
We find an averaged carbon atom distance of 2.82 Å from
the surface [18], in excellent agreement with the experi-

mental value to within 1.5%. The *internal* geometry of the
anhydride group [a-C versus anhydride and carboxylic O in
Fig. 3(a)] is also confirmed by DFT, although the splitting
of the vertical O positions is about 30% smaller than
experimentally observed. The *absolute* position of the
O=C—O—C=O group is, however, slightly closer to
the surface than found in the experiment [see Fig. 3(a)].
This difference is a consequence of the delicate balance
between the soft out-of-plane bending distortion of the
entire anhydride group and a weak bond of the carboxylic
O atoms to the Ag surface (see below). Indeed, if the
anhydride group is raised to the measured position, the
DFT energy increases by ~10 meV only. Our calculations
used standard double-zeta basis orbitals (including polar-
ization, DZP) for Ag and H, and triple-zeta orbitals (in-
cluding polarization) for O and C. In particular, for oxygen,
the use of a DZP basis yields positions of the O atoms
closer to the Ag substrate by ~0.1Å. This unusual basis-set
sensitivity also points to the softness of the bond between
the anhydride group and the perylene core. Hence the exact
determination of the z position of the O=C—O—C=O
group by DFT is intrinsically difficult and at the limit of
current DFT approaches [19]. Nevertheless, the good quali-
tative agreement between experiment and theory allows a
further analysis of PTCDA surface bonding.

   Which mechanism is responsible for the downward
bending of the terminal oxygen atoms? Figure 3(b) dis-
plays a cut through the DFT calculated total electronic
particle density (ρ) of the adsorbed molecule. Difference
maps of the electronic particle density ($\Delta\rho$ maps), i.e.,
electronic particle densities of the bonded PTCDA mono-
layer minus the bare Ag(111) surface and minus the free
(but distorted) PTCDA molecule [Figs. 3(c) and 3(d)], give
a clearer indication of charge redistributions. We observe
two effects: First, a transfer of spilled out charge from the
Ag surface into carbon π states on the perylene part of the
molecule, with a pronounced tendency of accumulation in
the space between the molecule and the metal [Fig. 3(d)];
second, a charge redistribution at the carboxylic O atoms
[Fig. 3(c)].

   The *first* effect clearly constitutes the spectroscopically
observed [5,7] bond between the Ag surface and the per-
ylene part of PTCDA. From the comparison of the hori-
zontal cut through this bonding region [Fig. 3(e)] and the
free PTCDA LUMO [Fig. 3(f)], it is apparent that this bond
is closely related to the former LUMO and therefore *ex-
tended*. This can be confirmed quantitatively by projecting
specific orbitals of the free molecule onto the full set of
adsorbate-substrate wave functions and summing over the
occupied states. By far the largest change in occupancy
occurs for the former LUMO: The LUMO-Ag hybrid
orbital is 1.4 eV broad, located about 0.1 eV below the
Fermi level, and it has accepted approximately 0.6 of an
electron from the metal, which is in qualitative accord with
experimental findings [5]. Notably, donation from the for-
mer highest occupied molecular orbital of the molecule

(now about 1.4 eV below the Fermi level) to Ag is insignificant.

The *second* effect [i.e., the charge redistribution in Fig. 3(c)] is closely related to the downward bending of the carboxylic O atoms and suggests the existence of a new, second bonding interaction between PTCDA and Ag(111). Along the axis of the C=O bond, we observe charge depletion. At the same time, charge is strongly accumulated in states with p_z-like symmetry. This is accompanied by a strong electron depletion in the Ag below the carboxylic O atoms. An electrostatic interaction of the negatively charged carboxylic oxygen with its image charge in the Ag(111) surface is certainly a significant factor. However, the smearing out of the p_z-like charge towards the first Ag layer indicates electron sharing between the carboxylic O atoms and the metal, hence a (weak) covalent bond, which can also be seen in the electronic particle density of Fig. 3(b).

How does this interaction between silver and O atoms fit into the picture of chemisorption via the perylene skeleton? The key is the mentioned charge transfer into the former LUMO of the molecule. This should result in a contraction of all C—C bonds in relation to which the LUMO is bonding, and a dilation of all C—C, C—O, and C=O bonds in relation to which the LUMO is antibonding [cf. the position of nodal planes of the LUMO in Fig. 3(f)]. Precisely this behavior is observed in the calculation. The contractions and dilations are in the range of 0.6% to 2.3%. Specifically, the C=O bond length increases from 1.21 to 1.24 Å upon adsorption. We note that this C=O bond weakening is also in agreement with vibrational spectroscopy data which show a strong redshift of the C=O stretch frequency on Ag(111). Filling of the LUMO therefore naturally promotes a tendency in the carboxylic oxygens to form an additional, *local* bond to the Ag surface.

Finally, we note that the dependency of the local on the extended chemisorption interaction is not a one-way relation. Any bond of the carboxylic oxygens to the Ag surface will itself tend to reduce the C=O double bond character and, indirectly, the π conjugation in the central perylene skeleton, leading to the *same* in-plane distortions of PTCDA as LUMO population does. Thus we conclude that both bonding interactions, although involving different parts of the molecule, go hand in hand in their mutual effect onto each other: Charge transfer into the LUMO promotes the Ag-O interaction, while the latter has the tendency to induce in-plane distortions in the perylene skeleton, which lower the energy of the LUMO and hence promote its filling.

In summary, from the experimentally determined vertical positions of elemental components of PTCDA on Ag(111), we set up a detailed model for the chemisorption of a large π-conjugated molecule with functional groups. Remarkably, we find two cooperative bonding interactions: a primary bonding on the perylene core which occurs by charge transfer from the Ag into the LUMO plus a local Ag-O interaction. This scenario bears similarities to the

Blyholder model [1]: Carbon-derived frontier orbitals participate in a strong charge exchange with the metal, and as a result, certain intramolecular bonds are weakened. In the case of PTCDA/Ag(111) this "weakening of the intramolecular bond" is seen as a lowering and secondary bonding of the carboxylic O to the Ag(111) surface.

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[13] The program DARE calculates the theoretical total PE yield on the basis of dynamical x-ray scattering theory (J. Zegenhagen, computer code DARE, 2002).

[14] The following nondipolar correction parameters of the PE cross sections were used: $Q_{O,C} = 0.31$ [15], $\Delta_O = -0.33$, and $\Delta_C = -0.22$ [16]. The influence of possible uncertainties of Q and Δ on d_c were found to be within the statistical errors of d_c, in agreement with Ref. [16].

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[18] The two molecules of the monolayer are in nonequivalent adsorption sites, with z positions deviating by up to ± 0.02 Å from the quoted averaged values. Figure 3 shows a molecule with an averaged geometry.

[19] Because of the weakness of the carboxylic O—Ag bond, differences may be also due to the details of the density functional [here: GGA functional by J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996)]. If, e.g., local-density approximation is used instead of GGA, the entire molecule is lowered by ~0.3 Å, in clear contrast to experiment.