Density-Dependent Reorientation and Rehybridization of Chemisorbed Conjugated Molecules for Controlling Interface Electronic Structure

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The adsorption of the molecular acceptor hexaazatriphenylene-hexacarbonitrile on Ag(111) was investigated as function of layer density. We find that the orientation of the first molecular layer changes from a face-on to an edge-on conformation depending on layer density, facilitated through specific interactions of the peripheral molecular cyano groups with the metal. This is accompanied by a rehybridization of molecular and metal electronic states, which significantly modifies the interface and surface electronic properties, as rationalized by theoretical modeling.

Understanding the fundamental mechanisms that determine the properties of interfaces between metals and conjugated organic materials is a key prerequisite for advancing the fields of *organic* and *molecular electronics*, where the (opto-)electronic function of devices depends critically on, e.g., charge density distribution [1,2], energy level hybridization and interface state formation [1,3,4], molecular conformation changes [3–6], and energy level alignment [5,7–9]. Additionally, it has been shown recently that the ionization energy of ordered molecular layers depends critically on the surface orientation of molecules, and that the energy levels at interfaces can be manipulated *via* molecular orientation [10]. However, it is commonly accepted that the orientation of a conjugated molecular monolayer with respect to a metal electrode surface is set for a particular material pair, only depending on the relative strength of metal-molecule and intermolecular interactions. If substrate-molecule interactions prevail, as for clean metal surfaces, at least the first molecular layer is found to be face-on [11–13]. Only multilayers are known to eventually adopt a different orientation [13–15] because the strong interaction with the metal is already screened by the monolayer. Here, we demonstrate the molecular density-dependent reorientation of an entire stable face-on monolayer to a stable edge-on conformation, which is achieved through balancing the surface energy in the two orientations by enabling strong hybridization of molecular and metal electronic states in *both* orientations through functional terminal groups. Particularly, the chemisorbed molecular state in the edge-on monolayer exhibits extraordinary electronic properties with a potential for huge application relevance, which is not the case for the face-on orientation.

Ultraviolet photoelectron spectroscopy (UPS) spectra were taken at the end station SurICat at BESSY II (Berlin). Kelvin-probe (KP) and thermal desorption spectroscopy (TDS) was done at the Graz University of Technology (Graz), and reflection absorption infrared spectroscopy (RAIRS) at the Zernike Institute for Advanced Materials (Groningen). All sample preparation steps and measurements were performed at room temperature and in ultrahigh vacuum. Metal single crystals were cleaned by repeated cycles of heating and sputtering and molecules were sublimed from pinhole sources. Further details can be found in the supporting information [16], where also details on the density-functional theory (DFT) calculations employed in this study are reported.

Hexaazatriphenylene-hexacarbonitrile (HATCN, chemical structure shown in the inset of Fig. 2) is a strong electron acceptor without an intrinsic dipole moment, which was here chemisorbed on Ag(111). The Ag(111) surface work function (Φ) changes due to HATCN deposition as shown in Fig. 1, determined independently by UPS and KP measurements. A pronounced deviation from the expected dependence of sample Φ on acceptor coverage (θ) is observed, as three regimes instead of two occur: (i) for low θ, Φ is essentially constant (from 0 Å to ~2.5 Å [17], highlighted in red (dark gray) in Fig. 1), (ii) followed by a strong and almost linear Φ increase by ~1 eV (from ~2.5 Å to ~8 Å, highlighted in black); (iii) finally a saturation of Φ is reached [beyond ~8 Å, highlighted green (light gray)]. The value of Φ changes from 4.4 eV [pristine Ag(111)] to 5.4 eV [26 Å HATCN/Ag(111)]. Commonly, the deposition of acceptors on metal surfaces involving net metal-to-acceptor electron transfer leads to the observation of regime (ii) from the very beginning, followed by regime (iii) [18]. Such a "delayed" increase of Φ, i.e., the additional appearance of regime (i), has not been reported before and cannot be rationalized on the basis of the Helmholtz-equation (or the Topping model
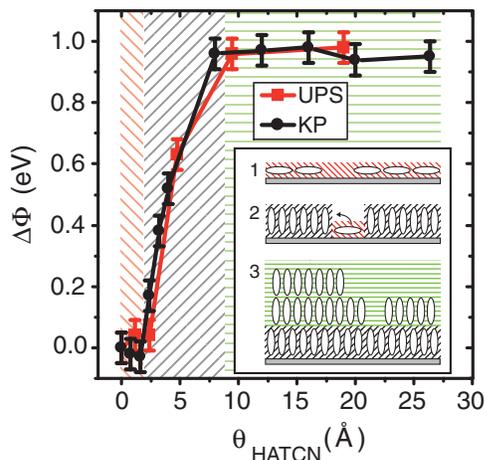
FIG. 1 (color online). Work function change $\Delta\Phi$ relative to pristine Ag(111) as a function of nominal HATCN thickness θ, obtained by UPS (red squares) and KP (black dots). The inset shows the proposed density-dependent orientation of HATCN on Ag(111). The color coding of the background shading represents the three different regimes referred to throughout the text: red (dark gray) = regime (i), black = regime (ii), and green (light gray) = regime (iii).

FIG. 2 (color online). TD spectra of mass 384 g/mol (HATCN) and mass 52 g/mol (HATCN fragment C_2N_2, see red rectangle in inset) for different θ on Ag(111). Data points were obtained by integrating the peak areas in the original TD spectra. The inset shows the chemical structure of HATCN.

including dipole-dipole depolarization effects [19]) when assuming any of the known growth models of conjugated molecules on metal surfaces. As regime (ii) sets in after completion of a face-on nominal monolayer of HATCN [20], a considerable electron transfer from the metal also into HATCN multilayers would have to be invoked, which is inconsistent with the present understanding of organic-metal interface energetics [21]. The situation is further complicated by the fact that several possible orientations of molecules on top of the first face-on layer may occur. Hence, without exact knowledge of the orientation of HATCN molecules on Ag(111) and its evolution with θ, an explanation for Φ throughout regimes (i)–(iii) is impossible.

The quantitative analysis of TDS experiments for various initial HATCN θ on Ag(111) is shown in Fig. 2, where the desorption of intact molecules ($m = 384$ g/mol) and HATCN fragments is plotted (C_2N_2, $m = 52$ g/mol); no other HATCN fragments were observed. One possible fragment of mass 52 is highlighted by the red rectangle in the inset of Fig. 2. Alternatively, only the terminal CN groups might desorb as radicals and react to form C_2N_2 [22]. Consistent with the evolution of Φ, Fig. 2 also displays three regimes: For θ up to ~2.5 Å no desorption of *any* HATCN fragments is observed throughout the entire accessible temperature range (up to 900 K). This is indicative of a HATCN layer strongly bonded to the Ag(111) surface. Between 2.5 and 8 Å, only desorbing C_2N_2 fragments are detected and virtually none of the molecules desorb intact. This shows that also in regime (ii) HATCN is strongly bonded to the metal, which would not be the case
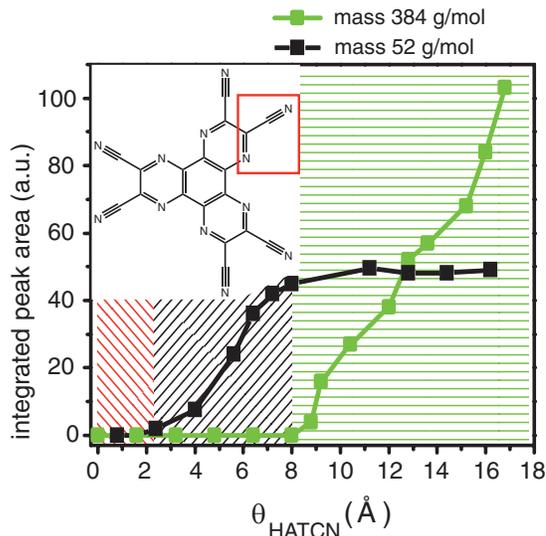
if they were part of a second layer. Instead, all molecules for θ up to 8 Å must be in direct contact with the Ag(111) substrate, and thus two different types of chemisorbed HATCN states (one for θ below 2.5 Å and one for thicknesses between 2.5 Å and 8 Å) exist. Beyond 8 Å an abrupt transition occurs: the thermal desorption (TD) signal intensity associated with fragments saturates and desorption of intact molecules starts. The latter signal increases roughly linearly with θ and is thus associated with relatively weakly bonded multilayers. The constant C_2N_2 signal implies that a HATCN layer equivalent to that of an initial θ of 8 Å exists below the multilayers.

The orientation and relative abundance of the two chemisorbed HATCN states in the first layer were further investigated by RAIRS. Here, the surface selection rules state that only those modes are observable, for which the dipole moment changes perpendicular to the surface [23]. HATCN in KBr serves as a reference for neutral molecules, and the region of the $C \equiv N$ stretching vibrations is shown in Fig. 3, with a strong mode at 2241 cm^{-1} and a weaker one at 2251 cm^{-1}. The RAIR spectra recorded *in situ* for sequential deposition of HATCN on Ag(111) are also shown in Fig. 3. Three characteristic peaks are observed, whose intensity changes as function of θ. From the very beginning a broad mode at 2185 cm^{-1} is seen (mode I), exhibiting a Fano-type line shape (for details see [16]), which is reminiscent of dynamical charge transfer between substrate and molecule [24]. The strong shift of this $C \equiv N$ stretching mode to lower energy compared to neutral HATCN indicates that the adsorbed molecule is negatively charged [25]. Mode I achieves its maximum intensity at $\theta \sim 2.7$ Å, where another mode at 2229 cm^{-1} (mode II)
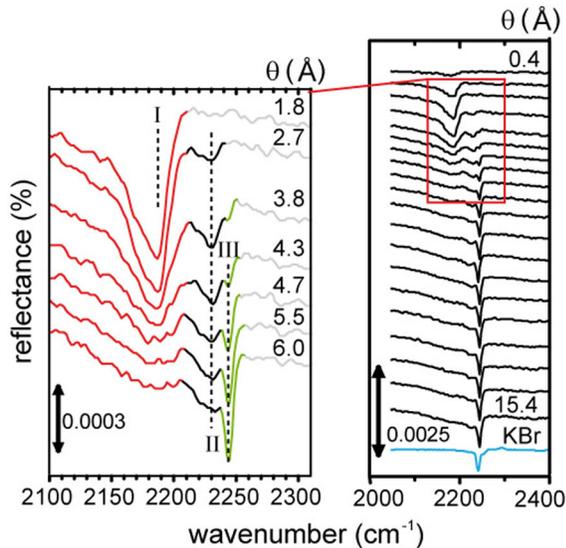
FIG. 3 (color online). Right: RAIR spectra recorded during
HATCN deposition on Ag(111) for the region of the $C \equiv N$
stretch mode. Left: Zoom of right part (denoted by the red
rectangle in the right panel) for θ up to 6 Å. The color coding
of the different spectral regions refers to the three regimes (i)–
(iii) used in the text.

appears in the spectra. For higher θ, the intensity of mode I
decreases, while the intensity of mode II saturates and can
still be well resolved at $\theta = 15.4$ Å. Starting at $\theta = 3.8$ Å,
a rather sharp mode at 2243 cm^{-1} (mode III) rises, which
is the only one that continuously keeps increasing for
higher θ. Mode I is attributed to face-on HATCN in direct
contact with the Ag(111) surface, consistent with [20]. In
this conformation the mode is IR active because of dy-
namical charge transfer between molecule and surface and
a nonplanar conformation of the molecule (*vide infra*). The
most striking observation is that this mode completely
vanishes for $\theta \sim 8$ Å, which is another clear indication
that the initial face-on HATCN chemisorbed state disap-
pears. The intensity decrease of mode I begins at ~ 2.5 Å,
similar to the onset of the desorption of HATCN fragments
in the TDS experiments. Mode II is associated with a
HATCN state in which the molecules stand edge-on (pos-
sibly somewhat inclined) on the surface. In that case, two
of the $C \equiv N$ groups are bonded to the surface, while the
other four only very weakly—if at all—are involved in the
molecular interaction with the surface. The smaller energy
shift of mode II relative to the mode of neutral HATCN in
KBr compared to mode I results from the bond weakening
due to charge transfer to the $C \equiv N$ groups, which is
partially compensated by C and N atoms now oscillating
"between" the Ag surface atoms and the rest of the mole-
cule. As mode III is very sharp and its position is close to
modes of HATCN in KBr it is attributed to originate from
multilayer HATCN, possibly superimposed by the vibra-
tions of the nonbonded $C \equiv N$ groups in the now edge-on
oriented monolayer.

The (re-)orientation of HATCN in the first few layers is
schematically summarized in the inset of Fig. 1, where
three regimes can be distinguished, as was already the case
in the initial observation of the Φ change in Fig. 1.
Therefore, a direct link between orientation of the mole-
cules and Φ can be established: In the initial stage of film
growth (from 0 Å to ~ 2.5 Å), the molecules are lying face-
on and Φ remains constant. With further deposition, the
chemisorbed face-on HATCN molecules reorient and are
incorporated into a monolayer, where the molecules are
aligned edge-on in a different chemisorption state. This
particular rearrangement leads to the large Φ increase until
saturation is reached at the end of regime (ii). We empha-
size that the reorientation cannot be induced by thermal
annealing, and that the face-on chemisorbed layer is stable
for several days as long as no further HATCN is deposited.
Experiments for HATCN deposited on Cu(111) substrates
yielded fully analogous results in terms of reorientation
and work function change regimes ($\Delta\Phi$).

To understand the mechanisms for the behavior of Φ, the
face-on and edge-on HATCN layers on Ag(111) were
modeled by DFT. For the face-on conformation of
regime (i) (assuming the structure from [20]) we find that
the charge transfer (CT) significantly outweighs Pauli re-
pulsion, giving a Φ change of $\Delta\Phi_{CT} = +0.7$ eV.
However, since the $C \equiv N$ groups at the periphery of
HATCN bend down towards the surface (Fig. 4(a) and
Ref. [20]), a dipole in the opposite direction is created,
yielding a molecular conformation related Φ change
$\Delta\Phi_{Mol} = -0.5$ eV. As a net result a small Φ increase of
$+0.2$ eV is obtained by DFT.

For the edge-on conformation of HATCN in regime (ii),
no experimental evidence for an ordered molecular layer
could be provided yet, which points to a disordered layer or
a very complex surface unit cell (as already found for bulk
HATCN *vide supra*). Thus a $2 \times 3\sqrt{3}$ unit cell containing a
single upright standing molecule was chosen for the cal-
culations (for details see [16]). In this conformation geo-
metric distortions of the molecule are small and $\Delta\Phi_{Mol}$
falls below $+0.1$ eV. The mechanism of CT between metal
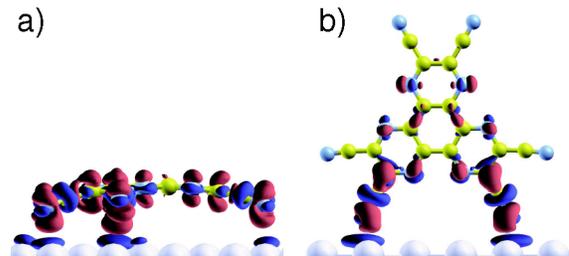and molecule is altered fundamentally by the reorientation.

FIG. 4 (color online). Charge rearrangements upon adsorption
in the face-on (a) and the edge-on (b) HATCN conformation as
inferred from DFT. Red (medium gray) indicates increased
electron density, blue (dark gray) electron density depletion.

Figures 4(a) and 4(b) show the charge rearrangements upon adsorption of HATCN in the two orientations. For the face-on conformation in regime (i) the whole molecule is involved in the interaction with the substrate, including σ electrons of the $C \equiv N$ groups as well as the entire π system. For the edge-on conformation, the CT becomes more localized on the "docking groups" (here: $C \equiv N$), similar to typical self-assembled monolayers [26]. The charge redistribution on the molecular backbone only plays a minor role. Yet the charge rearrangements occur over a larger distance than in the face-on conformation. In conjunction with the increased packing density and the vanishing $\Delta\Phi_{Mol}$, this results in an increase of Φ by +2.4 eV. The results for both regimes (i) and (ii) are at least in qualitative agreement with the experimental observations, as they show that the Φ change of the face-on monolayers is negligible compared to that induced by the edge-on layer. A better (i.e., quantitative) correlation between theory and experiment cannot be expected, particularly considering the unknown structure of the edge-on layer.

The microscopic origin of the density-dependent molecular reorientation must be sought in a subtle interplay of various effects. The σ-bonding strength between the $C \equiv N$ groups and the metal through the N lone pair can be expected to be larger for edge-on molecules; at low θ, it is, however, still favorable for HATCN to adsorb in a face-on geometry bringing all six $C \equiv N$ groups into contact with the metal, and maximizing the interactions with the substrate while at the same time minimizing the metal surface energy. Once the number of molecules is larger than needed to close the face-on layer, the total number of $C \equiv N$ groups in contact with the metal and their respective bonding strength is increased when at least part of the molecules change to edge-on. Thus, the presence of the functional groups at the periphery of HATCN facilitates the reorientation of the layer, while in their absence the second layer would just grow in a different orientation on the unchanged face-on monolayer. In our specific example, the structural change of the molecular monolayer was accompanied by a significant change in surface functionality; i.e., Φ for the edge-on layer was 1 eV higher than for the face-on layer or pristine Ag. In comparison, a monolayer of the widely used strong acceptor tetrafluoro-tetracyanoquinodimethane could increase Φ of Ag surfaces by only 0.6 eV [27]. This renders the high Φ surface an interesting candidate as hole injecting electrode in electronic devices, as the absolute Φ value of 5.4 eV parallels that of atomically clean Au, however, the electron "pushback" effect, which is detrimental for achieving low hole injection barriers on clean metal surfaces [2,7] is expected to be minimized by the surface termination with the molecule. Also, it might be interesting to evaluate whether interface dipoles reported for other organic-metal interfaces involve in part a contribution from a multilayer-induced reorientation of the buried monolayer in direct contact with the metal.

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