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Pentacene on Ag(111): Correlation of Bonding Distance with Intermolecular Interaction and Order

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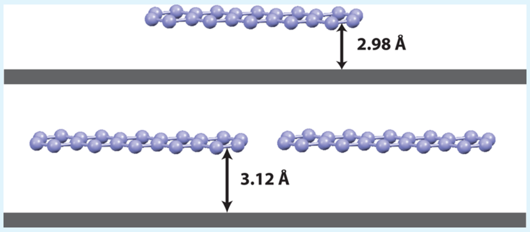

ABSTRACT: We report coverage and temperature dependent bonding distances of vacuum-sublimed pentacene (PEN) submonolayers on Ag(111) obtained by the X-ray standing wave technique. The average vertical bonding distance of 2.98 Å at room temperature for 0.50 monolayer (ML) coverage increases to 3.12 Å for 0.75 ML due to competing intermolecular and adsorbate−substrate interactions. In contrast, decreasing the temperature from 295 to 145 K does not impact the bonding distance despite the concomitant transition from a “liquidlike” to an ordered molecular arrangement. In combination with X-ray photoelectron spectroscopy results, we could identify “soft chemisorption” with a subtle balance of molecule−molecule and substrate−molecule interactions as being responsible for this special adsorption behavior. Thus our study sheds light not only on the interface between PEN and Ag(111), but also on fundamental adsorption processes of organic adsorbates on metals in the context of chemi- and physisorption.

KEYWORDS: *organic adsorbate, pentacene, bonding distance, soft chemisorption, intermolecular interaction, X-ray standing waves*

■ INTRODUCTION

Properties of interfaces between conjugated organic molecules (COMs) and metals are modern topics of fundamental research and are at the same time of key importance for the performance of devices in the field of *organic electronics*.[1,2] In this context, the first organic layer on a (typically metal) electrode in such devices is crucial for charge injection into the functional organic film and is, therefore, subject of intense research interest.[3−8] In particular, the bonding distance between the COMs forming the interfacial layer and the underlying metal is directly correlated with the interfacial bonding and electronic structure and, hence, critically impacts charge carrier injection.[4,5,9,10] However, despite extensive research efforts,[11−13] the adsorption behavior of COMs on metal substrates is still not understood comprehensively. Even for the prototypical COM pentacene (PEN) on Ag(111), the initial growth behavior was under debate for a long time[6−8] and could only recently be satisfactorily explained.[8] This was possible through applying a manifold of surface science techniques, including scanning tunneling microscopy (STM), ultraviolet photoelectron spectroscopy (UPS), near-edge X-ray absorption fine structure spectroscopy (NEXAFS), and thermal desorption spectroscopy (TDS).[6−8,14−18] From this, a unified picture of the initial growth at room temperature (RT) could eventually be drawn, evidencing a “liquidlike” *disordered monolayer* of flat-lying molecules with an ordered second layer growing on top.[6,8] At lower temperatures, however, already the first layer exhibits a high degree of order[18] and was successfully imaged by STM at 50 K.[8] Recently, it was found that such a remarkable growth is not unique to PEN, but was also found, for example, for perfluorinated pentacene (PFP) on Cu(111).[19,20] Note that, in the following, the term “liquidlike” is not understood in a strictly thermodynamic sense, but is used in analogy to the phrasing in literature, where no STM imaging of PEN (sub)monolayers on Ag(111) was reported to be possible at RT, most likely due to weak adsorption and thus molecule mobility under the STM tip.[6,8] In these studies, no topographic contrast of PEN could be detected but the micrographs just

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became more "noisy" compared to clean Ag(111). In contrast, the second (ordered) layer on top of the "liquidlike" monolayer could indeed be well imaged by STM even at RT.[6,8]

In a recent theoretical study, it was shown that the bonding distance of an ordered PEN monolayer on Ag(111) should increase in comparison to an isolated PEN molecule, as intermolecular interactions weaken the bonding between PEN to the substrate upon monolayer formation.[21] A dependence of the bonding distance on coverage was experimentally demonstrated for other COMs,[22−25] which is in line with the perception for epitaxially ordered adsorbates, suggesting that increasing coverage can be detrimental for the occupation of favorable adsorption sites.[22,25,26] However, the question arises whether this is equally true for intermolecular interactions in an amorphous "liquidlike" (sub)monolayer, like that of PEN on Ag(111), that is, whether the bonding distance similarly is expected to increase with coverage if no long-range order is adopted.

Here, we employed the X-ray standing wave (XSW) technique[27−29] to assess the bonding distance as a function of the PEN submonolayer coverage on Ag(111) both in the disordered phase at room temperature (RT) and in the ordered phase at low temperature (LT). Together with X-ray photoelectron spectroscopy (XPS), which is sensitive to the chemical environment of atomic species, the question of physisorption vs chemisorption for PEN/Ag(111), which is still controversially debated in literature,[8,14,21] is resolved. These considerations lead us to classifying the present system as intermediate case of "soft chemisorption" for all measured coverages and temperatures.

■ EXPERIMENTAL DETAILS

XSW experiments were carried out in back-reflection geometry at beamline ID32 of the ESRF (Grenoble, France).[30] The Ag(111) single crystal was cleaned by repeated Ar-ion sputtering and annealing cycles (up to 550 °C). PEN (Aldrich) was deposited with rates of about 0.25 Å/min (monitored with a quartz crystal microbalance) at a base pressure of 3×10^{-10} mbar. The evaluation of the thickness in terms of monolayers (ML) was done using the intensity ratio of C(1s) and $Ag(3d)_{5/2}$ XPS signals, photoemission cross sections, and molecular packing densities of PEN/Ag(111),[8] the error is estimated to ±0.10 ML. XPS was performed with an electron analyzer (Specs PHOIBOS 225 HV) mounted at an angle of 90° relative to the incoming X-ray beam. All preparation steps were performed at room temperature, the measurements at RT (295 K) and LT (145 K), respectively. The LT value was determined by the energy shift of the Bragg-reflection relative to RT due to thermal shrinking of the Ag(111) substrate with $d_{111} = 2.36$ Å at room temperature.[31] Analysis of the XSW results was done using the software package dare (developed at the ESRF). The error of the coherent fractions is estimated to ±0.10, the bonding distances have an error of ±0.05 Å. The XPS spectra in Figure 1 are measured with photon energies close to the Bragg-energies ($E_{Bragg} \approx 2.63$ keV) and with relatively high pass energies. Thus, the large widths of the C(1s) peaks (≈1.2 eV) might be mainly caused by experimental restrictions and hinder a detailed discussions of subtle changes in the spectra.

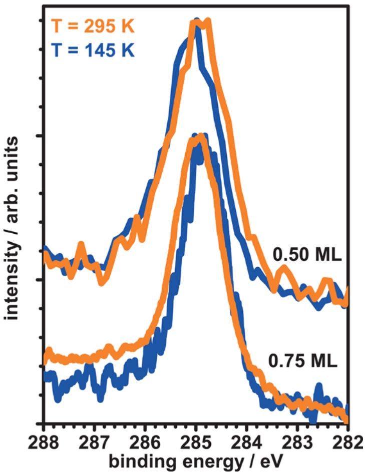

Figure 1. XPS C(1s) core level spectra of PEN on Ag(111). To avoid an impact of the standing wave field on the spectral shape, the spectra were measured with photon energies ca. 5 eV higher than the respective Bragg-energies ($E_{Bragg} \approx 2.63$ keV). The binding energy was calibrated using the $Ag(3d)_{5/2}$ core level as reference.

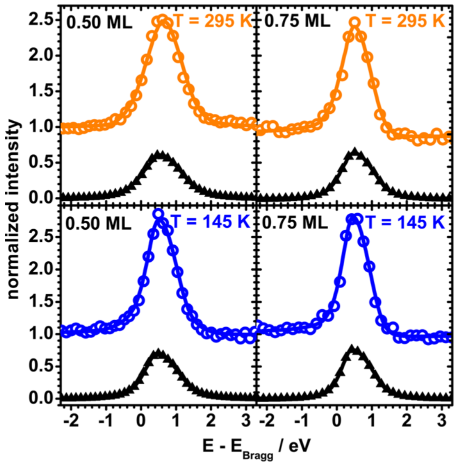

Figure 2. Photoelectron yield (open circles) of the PEN C(1s) core levels and reflectivity (triangles) as function of excitation energy (E) minus Bragg energy ($E_{Bragg} \approx 2.63$ keV) for two submonolayer coverages on Ag(111) measured at 295 and 145 K, respectively. Symbols correspond to the experimental data, and lines to the least-mean-square fits according to eq 1. The difference in E_{Bragg} between room temperature and low temperature was 7.40 eV.

■ RESULTS

The C(1s) core level XPS spectra of PEN on Ag(111) are displayed in Figure 1. For all measured coverages and temperatures, the rather symmetric peaks are centered at a binding energy of 284.9 ± 0.1 eV and no distinct splitting of the peaks is detected. The intensity of the C(1s) signals measured at various photon energies around the Bragg energy $E_{Bragg} \approx 2.63$ keV served as input for the XSW analysis (Figure 2). The X-ray standing wave photoelectron yield (Y_p) is given by[27,28]

$$Y_p = 1 + R + 2\sqrt{R}f_H \cos(\nu - 2\pi P_H) \qquad (1)$$

with R being the reflectivity and ν being the relative phase. It allows determining the coherent fraction (f_H), which is a measure for the degree of order of the adsorbate, and the coherent position (P_H), from which the bonding distance (d_H) can be determined by $d_H = d_{111}(n + P_H)$ with n being an integer. The corresponding values for PEN on Ag(111) are given in Table 1. The coherent fractions in our measurements are comparably high,[23,25,32] demonstrating that the molecules are lying rather flat on the surface. Cooling the samples increased the coherent fractions slightly, especially for the lower coverage (0.50 ML). There, cooling also increased the bonding distance by 0.06 Å, whereas changing the temperature did not

Table 1. Coverage in Monolayer (ML) Fraction, Coherent Fractions (f_H), Coherent Positions (P_H), and Bonding Distances (d_H) of PEN on Ag(111) for the Two Temperatures

	ML			
	0.50		0.75	
	295 K	145 K	295 K	145 K
f_H	0.65	0.80	0.65	0.70
P_H	0.26	0.29	0.32	0.33
d_H	2.98 Å	3.04 Å	3.12 Å	3.14 Å

influence the bonding distance at 0.75 ML coverage. For all samples, several spots on the substrate were measured and both, the coherent fractions and positions, exhibited only a small spread over these different spots. Noteworthy, we see a significant impact of *coverage* on the bonding distance, which we attribute to intermolecular forces that were suggested to lead to an increased bonding distance of the ML compared to an isolated molecule.[21] The transition from ordered to "liquidlike" behavior is reported to occur between 200 and 300 K,[8,18] indicating that our LT measurements at 145 K were performed on an already ordered PEN submonolayer. Our data point toward the impact of coverage on the bonding distance to be even higher in the disordered phase (surface height difference $\Delta d_H = 0.14$ Å for the two coverages) compared to the ordered phase ($\Delta d_H = 0.10$ Å). However, as the difference of 0.04 Å is close to the resolution limit of the XSW experiment we refrain from further elaborating on this finding.

DISCUSSION

Our results should be discussed in the light of available complementary literature data for PEN on Ag(111) and other substrates, and in the context of the bonding behavior of related molecules on metal substrates. The observation of a "liquidlike" PEN monolayer at RT is unique for Ag(111) substrates and was neither observed for PEN on Au(111)[33−35] nor for PEN on Cu(111),[19] where (sub)monolayer films are already ordered at RT and STM measurements were possible. The bonding distance of a PEN/Cu(111) submonolayer is 2.34 Å[20] and, thus, notably shorter than that of PEN/Ag(111) reported here (2.98−3.12 Å at RT). Perfluorination of PEN increases the bonding distances on Cu(111) to 2.98 Å for the carbon atoms and gives 3.08 Å for the fluorine atoms, respectively, pointing toward a significant distortion of the molecule.[20] Flat PFP submonolayers have a distance of 3.16 Å to the Ag(111) surface[32] which is very similar to the bonding distances of PEN on Ag(111) (Table 1). The carbon atoms in submonolayers of the pentacene derivatives 6,13-pentacenequinone (P2O) and 5,7,12,14-pentacenetetrone (P4O) on Ag(111) have bonding distances of 3.32 and 2.89 Å, respectively.[5]

For copper-phthalocyanine (CuPc), another widely investigated COM, the bonding distances on coinage metals have been explored in great detail, both as a function of the coverage and temperature. There, for the carbon atoms of physisorbed CuPc on Au(111), essentially no impact of coverage on the bonding distance (3.25 Å) was observed.[22,25] In contrast, on Ag(111), where CuPc turned out to be weakly chemisorbed, the carbon atoms did exhibit coverage dependent bonding distances between 2.99 and 3.09 Å.[22] The bonding distance of chemisorbed CuPc on Cu(111) substrates (with the expected strongest interaction), showed a strong dependence on the coverage, ranging from 2.53 to 2.82 Å.[25] In addition, also for other phthalocyanines, coverage dependent adsorption distances have been reported; however, there the situation is more complex as the molecules are either nonplanar in the gas-phase or exhibit strong adsorption-induced conformational changes.[4,23,24,36] Finally, for 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA), bonding distances to metals have been investigated in detail.[37−40] However, for PTCDA, the oxygen side groups play a key role in both bonding to the substrate and in the formation of the in-plane structure. The quadrupole moments in PTCDA, which mainly stem from the side groups, are much larger than those in PEN, leading to the unique packing of PTCDA with highly ordered structures and stacked layers on most substrates, irrespective of the adsorption strength.[41,42]

Our study on the adsorption distance of PEN on Ag(111) reveals a significant impact of coverage, but a negligible impact of temperature (i.e., lateral ordering) (Figure 3). This indicates that the bonding distance is influenced by the sheer presence of other molecules nearby rather than by their ordered packing. By nature, the monolayer structure is the result of the interplay of intermolecular and adsorbate−substrate interactions. For CuPc, as mentioned above, this fact has been discussed in the conceptual difference of physisorption and chemisorption, depending on the substrate's nature.[22,25,43] PEN on Ag(111) was suggested to be "almost physisorbed" based on UPS[14] and DFT-modeling,[21] whereas from NEXAFS and TDS a chemisorbed monolayer of PEN on Ag(111) with an activation energy for desorption of 2.14 eV[44] was suggested.[7] The absence of a split of the C(1s) XPS spectra for PEN/Ag(111) (Figure 1) was also observed for Au[45] (physisorption). In contrast, submonolayers of PEN on Cu(111) exhibited a splitting into two components separated by 0.65 eV due to chemisorption.[20] The bonding distance itself can be regarded as indicative of the adsorption strength,[10,25] and for PEN on Ag(111) d_H is in between the bonding distances of its oxo-derivatives with P2O being physisorbed and P4O being chemisorbed.[5] Thus, for the present case of PEN on Ag(111), the term "soft chemisorption" may be appropriate. Moreover, even the highest value of our measured d_H (3.14 Å) is significantly smaller than the sum of the van-der-Waals-radii of C and Ag (3.42 Å). However, taking the sum of the van-der-Waals-radii as limiting value for physisorbed COMs on metals is not straightforward[40,46] as the transition between physi- and chemisorption is, indeed, smooth. The binding energy of the C(1s) core level (Figure 1) is (within the error margin) neither influenced by the coverage nor by the temperature, which agrees well with the notion of weak interaction.

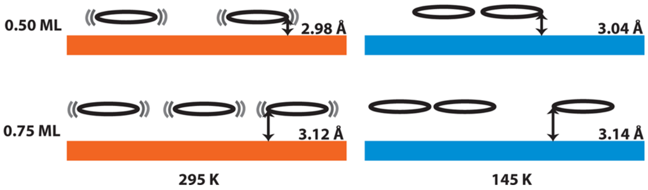

Figure 3. Sketch of vertical adsorption distances of PEN submonolayers with the "liquidlike" layer at room temperature (left panel) and the ordered phase at low temperature (right panel) for the two coverages (0.50 and 0.75 ML) investigated in this work.

Soft chemisorption might also explain why the first PEN monolayer cannot be imaged by STM at RT on Ag(111): the cases of physi- and chemisorption on Au(111) and Cu(111) respectively, present energetic minima which are either clearly dominated by the molecule−molecule or the substrate-molecule interaction. For soft chemisorption, however, these forces are similarly important and, given a sufficiently high thermal energy, this interplay enables the PEN molecules to move about, leading to the "liquidlike" behavior. Further insight into the occurrence of soft chemisorption comes from a comparison of PEN and PFP. The single crystal structures of these molecules are, in the absence of a substrate, merely determined by the intermolecular interactions. Here, the quadrupole moments of PFP,[47] which are induced by the strong carbon−fluorine intramolecular polar bonds (IPBs),[48] lead to a distinct difference in the structures of PEN and PFP: All polymorphs of PEN exhibit a "classical" herringbone arrangement with herringbone angles close to 50° (refs 49 and 50), whereas the IPBs of PFP lead to more stacked molecular planes with a herringbone angle close to 90° (ref 51) Interestingly, however, a recent STM-study[19] demonstrated that, if adsorbed on surfaces, PFP can likewise form a "liquidlike" monolayer despite its strong IPBs. As fluorination of PEN decreases the interaction with noble metal surfaces[20,52] the case of soft chemisorption seems now shifted from Ag(111) to the more reactive Cu(111). This is also clearly seen by the similarity of the bonding distances found for PEN/Ag(111) (2.98 to 3.14 Å) and PFP/Cu(111) (2.98 and 3.08 Å for the carbon and fluorine atoms, respectively). As much as the adsorption strength influences the monolayer structure, for both PEN and PFP, the structure in the multilayer regime (several nanometer nominal thickness) does not depend very critical on the substrate and is again dominated by the strength of intramolecular quadrupole moments: On all (111)-surfaces of coinage metals PFP multilayers exhibit π-stacking,[53] whereas PEN multilayers adopt a herringbone arrangement.[7,34,54]

CONCLUSIONS

Our results represent a further step forward in revealing the initial growth mode of PEN on Ag(111) by measuring the coverage and temperature dependent bonding distances. We demonstrated that intermolecular interactions impact the bonding distance even for "liquidlike" monolayers. Consequently, the adsorption height of PEN on Ag(111) does not significantly depend on the lateral order but on the coverage. The balanced interplay of molecule−molecule and substrate−molecule interactions of soft chemisorption is identified as the reason for the particular growth mode of PEN on Ag(111) with a "liquidlike" monolayer at room temperature which becomes ordered at low temperature. Given the similarities for PFP on Cu(111), the same reasoning might also be applicable in other cases of functional COMs on metal surfaces.

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Notes

The authors declare no competing financial interest.

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