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Photoelectron Spectroscopy (PS) and Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy have been used to investigate the occupied and empty density of states of biphenylene films of different thicknesses, deposited onto a Cu(111) crystal. The obtained results have been compared to previous gas phase spectra and single molecule Density Functional Theory (DFT) calculations to get insights into the possible modification of the molecular electronic structure in the film induced by the adsorption on a surface. Furthermore, NEXAFS measurements allowed characterizing the variation of the molecular arrangement with the film thickness and helped to clarify the substrate-molecule interaction. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4975104]

I. INTRODUCTION

Biphenylene (Figure 1) is a cyclic hydrocarbon formed by two benzene rings and a cyclobutadiene ring. Despite the expected antiaromaticity due to its electronic structure with $4n\pi$-electrons (according to the Hückel rules), biphenylene is stable[1] but still more reactive than benzene.[2] Its characteristics, halfway between aromatic and antiaromatic molecules, its uncommon photophysical properties,[3] and its anomalous high conductivity shown in thin polyphthalidylidene biphenylene films[4] make biphenylene the target of many experimental and theoretical studies.[4–8]

Biphenylene is also considered an important building block of molecular materials, a novel class of materials suitable for a variety of technological applications, due to the possibility to tune the electrical and optical properties[9–11] by choosing proper building blocks and surfaces.

In this context, biphenylene can be regarded as the very initial precursor of a 2D porous graphene-like molecular network, called biphenylene carbon (BPC). Predicted for the first time by Balaban,[12] BPC is characterized, theoretically, by an intrinsic band gap and bands with delocalized frontier orbitals.[13,14] Biphenylene sheets, originating from biphenylene dimers,[15] have also been hypothesized and their one-dimensional derivatives, like ribbons and tubes, have been theoretically investigated.[16]

The most reliable and promising approach to grow this kind of covalently bonded carbon materials is a bottom-up procedure, exploiting the surface-confined self-assembly of functionalized molecular building blocks and their interaction with appropriate surfaces (generally coinage metal substrates). Covalently bonded materials show superior thermal and chemical stability with respect to highly ordered hydrogen-bonded porous carbon networks[17–19] and to other self-assembled structures given by surface metal coordination[15] or aromatic coupling motifs.[20]

In order to investigate the behavior of biphenylene as a precursor of 2D structures like BPC, we have performed a preliminary characterization of biphenylene films deposited on a Cu(111) substrate, through Photoelectron Spectroscopy (PES) and Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. In a previous experimental and theoretical work,[21] we studied the electronic structure of biphenylene in the gas phase, disentangling the contribution of each carbon sites, C_α, C_β, and C_γ to the molecular electronic structure (see Figure 1). In the present study, we have investigated the occupied core and valence levels as well as the non-occupied states of biphenylene in films of different thicknesses to elucidate the molecule-substrate interactions (low coverage films) and the molecule-molecule interactions (high coverage film). For a deeper comprehension of the intermolecular interactions, the results of the thicker film have been also compared to the previous gas phase measurements and to Density Functional theory (DFT) calculations simulating the total density of states (tDOS) and the partial density of states (partial DOS) from π and σ orbitals for a single biphenylene molecule. Moreover, NEXAFS experiments at different geometries with respect to the impinging light have been performed on films of increasing thickness, in order to ascertain the molecular orientation in the deposited layers, which is relevant for their implementation in molecular electronics.

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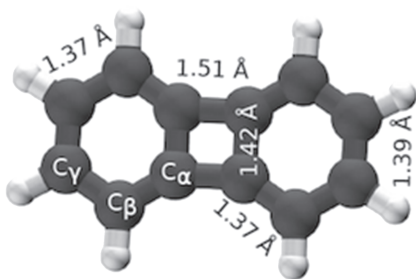
FIG. 1. Biphenylene molecular structure with theoretical C–C bond lengths. Three non-equivalent carbon atoms can be identified as follows: C_α, C_β, C_γ (see Ref. 21).

II. EXPERIMENTAL DETAILS

Biphenylene films of different thicknesses were characterized at the photoemission branch of beamline I311 at the MAX IV Laboratory, the Swedish synchrotron radiation facility, in Lund. I311[22] was an undulator-based soft X-ray beamline (30–1500 eV), equipped with a modified Zeiss SX-700 monochromator. The spectroscopy end-station was equipped with a hemispherical electron energy analyzer (Scienta SES 200) for high resolution PES and NEXAFS.

The pressure in the analysis chamber and in the preparation chamber, during the experiments, was kept in the low 10^{-10} mbar range.

Standard procedure of Ar^+ sputtering (1 kV, 20 min) and annealing (820 K, 20 min) was adopted to clean and reconstruct the Cu(111) crystal surface, until no signal from contaminations was detected.

The biphenylene powder (Sigma-Aldrich, 99%) was placed in a glass tube connected to the preparation chamber through a leak valve and to a pumping system. Prior deposition, biphenylene was outgassed at a temperature around 373 K. Biphenylene was successively evaporated at the same temperature and deposited on the freshly prepared Cu(111) crystal, cooled to 90 K by liquid nitrogen. This temperature allows a sufficient sticking of the molecule and thus the growth of films of different thicknesses. The pressure in the preparation chamber during deposition was in the low 10^{-8} mbar range.

The thickness d for the different films was evaluated considering the attenuation of the Cu 3p peak intensity according to the Lambert–Beer attenuation law: $I/I_0 = e^{-d/\lambda}$, with I_0 and I indicating the intensity of a spectroscopic line from the clean substrate and after the molecule deposition, respectively, and λ being the electronic inelastic mean free path for the considered kinetic energy. The film thicknesses of the analyzed samples have been estimated to be ~100 Å (high coverage), ~30 Å (intermediate coverage), and ~7 Å (low coverage). We also show the C 1s spectrum obtained on a biphenylene monolayer, with an estimated thickness of ~3 Å.

C 1s spectra were recorded with a photon energy of 400 eV at normal emission (NE) geometry (sample in front of the analyzer). The valence spectrum was acquired with a photon energy of 130 eV in normal incidence (NI, sample surface normal to the photon beam) and NE geometry. The binding energies (BE) of the photoemission results have been calibrated with respect to the Cu Fermi level, with the exception of the high coverage C 1s spectral peak position. This peak

has been calibrated with respect to a calibrated valence spectrum, being all Cu peaks hidden under the thick biphenylene film. The photon energy of the NEXAFS spectra was calibrated considering the first and second order of the Cu 3p core level. The overall resolution was 90 meV for the C 1s spectra, 33 meV for the valence, and 30 meV for the NEXAFS spectra.

The theoretical valence band spectra shown in this work have been shifted in BE by −1.9 eV in order to align the theoretical Highest Occupied Molecular Orbital (HOMO) with the experimental peak, due to the different energy references used in the gas phase and DFT calculations (vacuum level) and surface measurements for solid/metal samples (Fermi level). The alignment allows for an easier comparison with the film data.

The samples were scanned during measurements, in order to prevent the beam to damage the deposited films.

III. COMPUTATIONAL DETAILS

DFT calculations were performed to obtain detailed insights into the electronic structure. The geometry of the biphenylene molecule was optimized by means of DFT calculations with the hybrid functional B3LYP,[23] using the GAUSSIAN 09 program.[24] The 6-311G(d,p) plus polarization basis sets were used for all the atoms.[25] For the eigenstate spectra used to simulate the valence band PES, the projected Density of States (pDOS) was computed with the c^2-method, which is frequently employed to yield the atomic contributions to the total DOS (tDOS).

The pDOS was obtained by including the eigenvalues corresponding either to the π or the σ orbitals. The tDOS and partial pDOS curves of the valence band, representing the theoretical PES, were broadened by Gaussian functions, to facilitate the comparison with the experiments. Gaussian curves with a FWHM of 0.23 eV were used.

To compute the propagation of a 1s electron into an unoccupied p-type orbital, e.g., an excitation as it appears in NEXAFS measurements, the Transition Potential Approach (TPA) was used in the StoBe2007 package.[26] The Becke exchange and the correlation functional by Perdew computed the many-body effects,[27,28] while the core-excited electron was described by the igloo-III basis set.[29]

IV. RESULTS

In Figure 2 we show the C 1s spectra of biphenylene films at high, intermediate, low, and monolayer coverages. Only one very intense peak characterizes the photoemission spectra for the different coverage regimes, despite the three non-equivalent atoms in the molecule (Figure 1). However, the main peak line shapes and positions exhibit an evolution as a function of biphenylene thickness. The monolayer (Fig. 2(d)) and low coverage (Figure 2(c)) peaks are asymmetric and centered at 284.5 eV and 284.6 eV, respectively. Upon further biphenylene depositions, the peak becomes symmetric and shifts to higher BE, being centered at 284.9 eV for intermediate coverage (Figure 2(b)) and 286 eV for high coverage (Figure 2(a)).
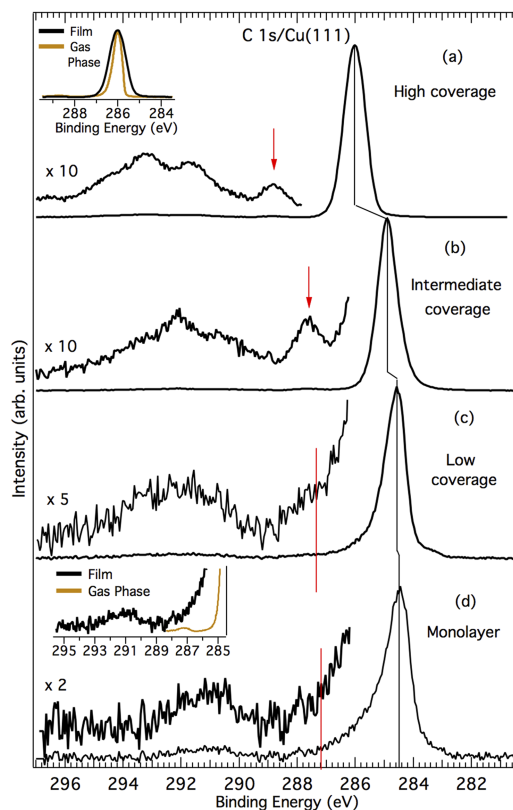
FIG. 2. C 1s photoemission spectra of a biphenylene film of (a) high (100 Å), (b) intermediate (30 Å), (c) low (7 Å), and (d) monolayer coverage (3 Å) acquired with hν = 400 eV and an overall resolution of 90 meV. Biphenylene shake-up regions have been enlarged for the sake of clarity. Red arrows and lines indicate the position of the shake-up peak at about 2.7 eV from the main line. *Insets*: (a) comparison between the C 1s spectra of the high coverage film and of biphenylene in the gas phase; (d) comparison between the monolayer and the gas phase shake-up regions. The gas phase spectrum is from Ref. 21.

The monolayer and low coverage C 1s photoemission lines show the typical asymmetric shape, also observed for other low coverage films of carbon-based molecules on metallic substrates.[30–32] The asymmetry is usually ascribed to the inelastic scattering of the photoelectrons with electron-hole pairs in correspondence of the Cu Fermi level (E_F), i.e., the high density of state at E_F allows for shake-up transitions from states just below E_F to empty states just above E_F. At higher film thicknesses, the increased coverage on the surface and then the quenched molecule-substrate interaction make the inelastic scattering less favorable and the line shape may become more symmetric, as observed in Figure 2.

The C 1s BE shifts of the different biphenylene coverages can be attributed to the more effective core hole screening in the lower coverage situations by the metal crystal, resulting in a lower BE for the emitted photoelectron. For thicker films, the electron screening of the core hole by the metal is instead less effective and the BE of the core level peak increases, giving a Δ(BE) of 1.5 eV for the high coverage sample, with respect to the monolayer sample.

By the comparison of the shake-up regions (i.e., above 287 eV), important information on the interactions between the adsorbed molecules and the substrate can be deduced. In the figure, shake-up regions have been enlarged for the sake of clarity. While in the monolayer and low coverage spectra

the shake-up region is made of a broad peak centered at about 291 eV and 292 eV, respectively, in the intermediate and high coverage cases shake-ups show rather complex and structured features.

A notable difference is the disappearance, in the monolayer and low coverage C 1s spectra, of the shake-up feature (indicated by red arrows and lines in the figure) at about 2.7 eV from the main peak, instead clearly seen for the films of higher biphenylene coverage and in the biphenylene C 1s gas phase, from Ref. 21, shown in the inset of Figure 2(d).

This shake-up at 2.7 eV from the main peak can be attributed to HOMO-LUMO (Lowest Unoccupied Molecular Orbital) transitions. The HOMO-LUMO gap of biphenylene has been estimated in previous optical and near UV absorption studies to be 3.5 eV.[33,34] The smaller value of such transitions obtained when comparing the optical absorption with the XPS or NEXAFS results is quite common and it is mainly due to the effects of the core hole on the electronic structure of the molecule. First of all, the presence of the core hole (created in XPS and NEXAFS processes) represents an electrostatic attraction that affects the density of states, shifting the empty states closer to the HOMO. Moreover, the core hole can perturb and break the symmetry of the molecule, inducing a significant modification on the electronic structure with possible new transitions available in the ionized/excited state. This has been clearly shown in the study by Enkvist *et al.*[35] about C_{60}, where the main contribution to the shake-up at 2.2 eV from the C 1s main line is ascribed to new excitations involving the HOMO-LUMO transition of the core ionized molecules. In summary, the first shake-up peak at 2.7 eV from the C 1s main line of biphenylene can be attributed to the HOMO-LUMO transitions, keeping however in mind that the shake-up spectrum gives information about the molecular electronic structure in the excited state that can be characterized by a new kind of possible transitions.

It is important to mention previous experimental and theoretical studies[35–37] that have investigated in great details the shake-up spectra of molecules of increasing complexity, from small aromatic molecules such as benzene, naphthalene, and acenaphthylene to C_{60}. These works explained some characteristic features observed in the photoelectron spectra of such molecules. The first shake-up structure, closest to the main line, would be due to HOMO-LUMO transitions that include also non-local (or interring) charge redistribution from the boundaries of the molecule towards the core-hole site, i.e., from a ring or part of the molecule far away from the core hole. The shake-up intensities at high BE (about 6 eV from the main line) would correspond to local (intraring) excitations accompanying the photoelectron process, i.e., charge transfer from the core-hole site and the neighboring sites.

Then, the lack of the low binding energy shake-up and the asymmetric line shape of the C 1s spectrum for monolayer and low coverage biphenylene films is considered as a significant modification of the molecular electronic structure, due to the interaction with metallic Cu(111) surface which, as already mentioned, would allow transitions from just below to just above the Fermi edge. On the contrary, the presence of this shake-up in all the higher coverages as in the gas phase

indicates how the films recover a molecular character when the interaction with the substrate becomes more and more negligible.

The high coverage C 1s spectrum (Figure 2(a)) is compared with the gas phase spectrum from Ref. 21 (inset of Figure 2(a)), since at this coverage the substrate contribution is minimized and the film would retain most of its molecular character. We can see that the C 1s peak in the gas phase spectrum is much narrower (FWHM = 0.5 eV) than in the film (FWHM = 0.9 eV). This observation can be only partially explained with a somewhat better resolution in the gas phase PES results (75 meV), than in PES of adsorbed films (90 meV). In fact the two peaks are also characterized by a clearly different line profile: symmetric for the film and asymmetric for the gas phase. As already shown in our previous work[21] and similarly to biphenyl[38] and naphthalene,[39] the asymmetry of the gas phase line is ascribed to intramolecular vibrations, which give rise to an asymmetric tail. In the film the situation is different, since many of the intramolecular vibration modes become frustrated. Furthermore, measurements of the films were carried out at low temperature of the Cu substrate, with a reduced vibrational contribution. This, on the other end, could be distributed among new lower energy modes arising from intermolecular and substrate-molecule interactions, resulting in a broader and more symmetric C 1s line shape. Moreover, considering that the molecular arrangement in thick films can be quite complex, aware of the proposed structure for biphenylene crystals, with three molecular ribbons of two different orientations for a unit cell (similar to a herringbone structure),[40] we could ascribe the broad C 1s line for the thick film to chemically shifted components due to non-equivalent carbon atoms.

Valence spectra acquired at low coverage and intermediate coverage are dominated by the strong Cu valence band features, which completely hide the biphenylene valence photoemission peaks in the low BE region. A general shift towards higher binding energies, when biphenylene thickness increases, characterizes the remaining valence peaks. This is ascribable to the screening of the underlying Cu substrate, as already seen in C 1s spectra. However, since no other information could be extracted from these data, they are not shown.

In Figure 3 we show, instead, the valence spectra of a high coverage film, acquired in NE and NI, with θ (angle between the polarization vector **E** of the incident radiation and the surface normal **n**) of 40° and 90°, respectively (see the inset in Figure 3). The photon energy of 130 eV used for the acquisition allowed to measure almost at the maximum surface sensitivity condition, with an electron inelastic mean free path of about 10 Å.[41] In the same figure, we report the calculated tDOS for the gas phase molecule, where we show the total as well as the π and σ pDOS.

A general good agreement in the position of the peaks is observed between the film, gas phase, and calculated spectra, even though the film lines, like for the C 1s core level, are affected by a significant broadening. The relative positions in BE of the structures from D to I recall those of the theory and gas phase spectra. The not perfect correspondence among the peak intensities is due to several reasons, like different photoemission cross sections at the two photon energies
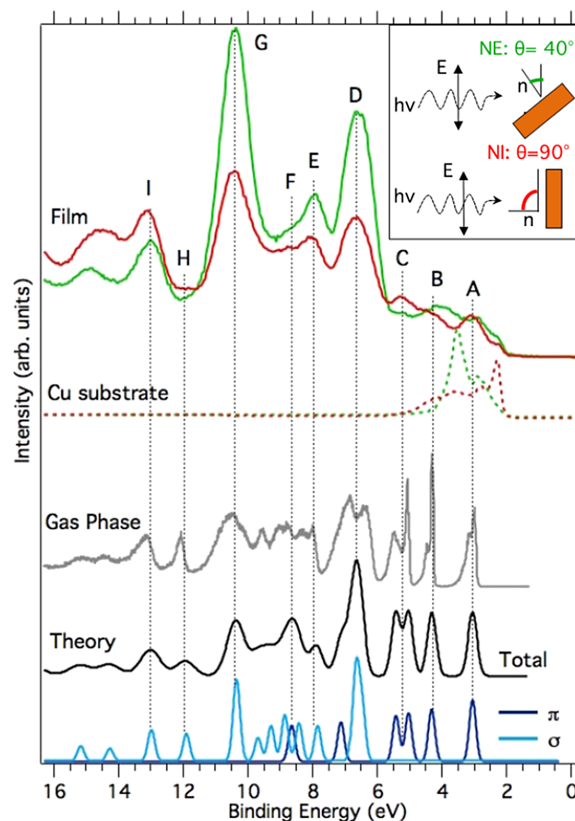

FIG. 3. Valence spectra of the high coverage biphenylene film in the two acquisition geometries of NE (green) and NI (red). The spectra of the clean Cu(111) acquired at the same geometries are shown as dashed lines. The gas phase valence spectrum, the tDOS (from Ref. 21), and the π and σ resolved pDOS are also displayed. Film and gas phase spectra were acquired with hν = 130 eV and 50 eV, respectively. *Inset*: schematic representation of the acquisition geometries indicating the angle θ between the surface normal **n** and the direction of the polarization vector **E** of the light.

used (130 eV for film and 50 eV for gas phase) and different experimental setups used for the film characterization, allowing the enhancement of photoemission intensity for orbitals of certain symmetry at NE or NI geometries (as discussed in the following).

Contributions from the Cu substrate are visible in correspondence of the most intense Cu valence peaks: at 3.5 eV in NE and at 2.2 eV in NI. The photoemission contributions from the Cu(111) substrate can also explain why the HOMO, HOMO-1, and HOMO-2 peaks (A, B, C in Figure 3) in the film are less resolved and less intense than in the gas spectrum, even at such a coverage that would correspond to a film of molecular character. Moreover, considering the high coverage of the film, the intensity of the still observable substrate valence features suggests that the film is not uniform.

We can exploit the different intensities of the valence peaks for the two different geometries to obtain information about the orientation of the molecules on the surface. In fact, as it is well known, in planar organic molecules like biphenylene, σ and π orbitals have well defined directions in space: in plane and perpendicular to the molecular plane, respectively. Then, the synchrotron linearly polarized light can be used to probe the direction of molecular orbitals, i.e., the orientation of the molecules in the film. This is generally done with NEXAFS,[42] since the observed resonances naturally represent the excited

non-occupied π and σ orbitals. However, it is also possible to determine the orientation of the molecules by enhancing the different contributions from π and σ orbitals to the valence PES structures varying the orientation of the sample with respect to the incident light (e.g., the work of Åhlund *et al.*[43]). We performed DFT simulations of our system (Figure 3, bottom spectrum) revealing that peaks due to π orbital contributions (A, B, C) are slightly more intense in NI with respect to NE, even if A, B, and C intensities are distorted, especially in NE, by Cu valence structures. However, in the region from 6 to 12 eV, in absence of any Cu valence contributions, peaks due to σ orbitals (D, E, G) show the opposite behavior. Considering that the polarization vector **E** is perpendicular to the light direction (and changes with respect to the surface depending on the incidence angle of the light), in the high coverage case the molecules appear to be standing on the surface. High BE peaks (H, I) deviate from this behavior because of the stronger contribution from the background. The estimated molecular orientation in the film is also confirmed by our NEXAFS measurement.

NEXAFS results of the thicker biphenylene film, taken at NE geometry and presented in Figure 4, are compared to the gas phase spectrum and theoretical NEXAFS simulations for a single molecule, showing the total transition intensities and the partial transition intensities from π* and σ* resonances. The film spectrum shows very distinctive features: those around 285 eV, 287.5 eV, and 289 eV are originated from the electron transition from the C 1s to π* orbitals, while from 293.5 eV and higher photon energies all features are due to both π* and σ* resonances. Apart from a general difference in peak intensities, the peaks of the film spectrum coincide well with those of the gas-phase and of the theoretical spectra. The features at 285

eV and 289 eV and the high photon energy region are in very good agreement, but the peak at 287.5 eV is more intense in the gas phase. The asymmetric tail on the higher photon energy side of the main peak, due to the contribution of the C_β atoms (Ref. 21), is also present in the film. The resemblance of the gas phase, theoretical, and experimental NEXAFS spectra confirms the molecular character of the thick film, as already deduced from valence band photoemission and observed for other molecular films.[44]

For an estimation of the molecular arrangement, we performed NEXAFS measurements at different orientations of the sample with respect to the incident light, for each obtained coverage (high, intermediate, and low). In Figure 5(a) we display the NEXAFS data for the high coverage film, already shown in Figure 4, together with the NI geometry. These spectra show that in the thicker film the molecules arrange themselves according to a preferential direction. In fact, the first two π* resonances at about 285.0 eV and 287.0 eV are enhanced in NI, indicating, as already anticipated by the valence results, molecules preferentially standing on the surface of the substrate. Considering that the dichroism of the high coverage resonances is not so strong, and being aware of the proposed molecular order forming a herringbone-like structure in biphenylene crystals, we suggest that the molecule could have a quite complex arrangement.[40]

Subsequently, we studied the molecular arrangement as a function of the film thickness on a low coverage film (7 Å thick) and on an intermediate coverage film (30 Å thick), at the normal (NI) and the grazing incidence (GI, θ = 20°) geometries.

For the low coverage (Figure 5(b)), a strong polarization dependence is observed, with an opposite trend with respect to the high coverage, indicating a tendency for the molecules to adsorb lying on the surface.

In order to have a more accurate estimation of the molecular orientations, we used the formula[42]

$$I_{\pi^*} = A \left(\cos^2 \theta \cos^2 \alpha + \frac{1}{2}\sin^2 \theta \sin^2 \alpha \right) \quad (1)$$
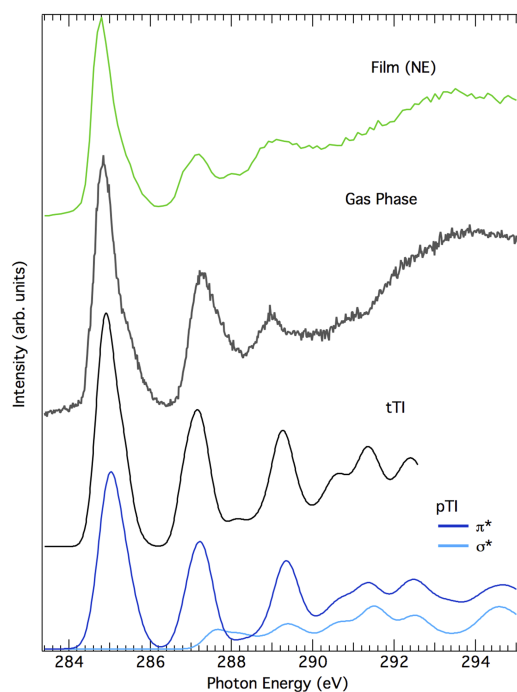

FIG. 4. Biphenylene thick film NEXAFS spectrum in NE geometry. The film spectrum is compared to gas phase results and DFT calculations showing the total transition intensity (tTI) and the partial transition intensity (pTI) for the π* and σ* contributions.
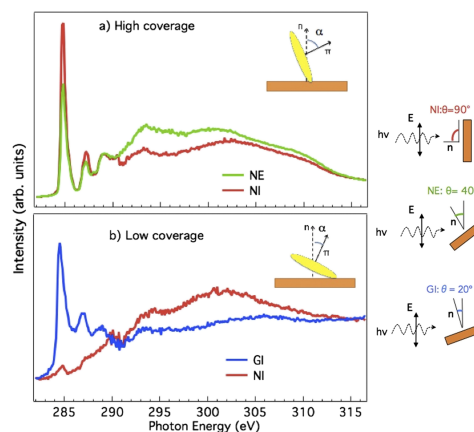

FIG. 5. Polarization dependent NEXAFS for two film thicknesses: High coverage (a) and low coverage (b) films. Each film was measured for different values of θ, the angle between the polarization vector **E** of the incident radiation, and the surface normal of the Cu(111) sample. The geometries, shown in the schematic representation, are as follows: θ = 90° (NI) and 40° (NE) for high coverage and θ = 90° (NI) and 20° (GI) for low coverage.

describing the intensity of the first π^* resonance as a function of the angle θ for a substrate with a threefold symmetry, such as Cu(111). For this kind of symmetry, there is no dependence from the surface azimuthal direction, thus the only unknown parameters are the angle α that the π orbitals form with the normal to the surface **n** and the multiplying constant A. Solving the system with the values of I_{π^*} and θ obtained from the high coverage and low coverage experiments, we determine $\alpha = 66° \pm 5°$ and $20° \pm 5°$, respectively (see the schematic representations of the molecular arrangement in Figure 5). The reported uncertainties take into account the angle reading and the background normalization. However, these values have to be considered quite speculative since a more accurate angle dependent study would be necessary for defining more reliable results.

In Figure 6(a), the NEXAFS results obtained from the intermediate coverage sample are shown. As we can see, there is no remarkable dependence of the π^* and σ^* resonances on the **E** direction, in the two geometries of NI and GI, thus several hypotheses can be proposed. In fact, it could imply that the film is not characterized by a preferential molecular orientation or disordered. However, if this were the case, there would be no reason to observe a resonance intensity dependence from the **E** direction, i.e., an ordered arrangement, for the high coverage, as we indeed do. A more suitable explanation would be considering biphenylene molecules for the intermediate coverage arranged, on average, at $\alpha \approx 55°$. In fact at this angular value, known as the magic angle, the intensity of NEXAFS resonances is indistinguishable from that given by a disordered system.[42]

Another possibility would be interpreting the intermediate coverage situation as a transition phase. Biphenylene molecules rise from the low coverage lying to the high coverage standing configuration, gradually moving from one position to the other. Therefore, progressively different oriented contributions would give the same result of a set of randomly disposed molecules and would explain the arrangement observed for the high coverage.

We then performed an annealing on the intermediate coverage film, heating the substrate from the LN$_2$ temperature to 223 K for about 5 min and then we cooled it down again to 90 K. From the NEXAFS spectra acquired thereafter (Figure 6(b)), we saw that the line shapes are very similar to the spectrum at the low coverage (Figure 5(b)) and the polarization dependence is the same. Applying Equation (1) to this system, we obtain $\alpha = 26° \pm 5°$, very close to the average angle measured for the low coverage. Hence we estimate that, after this treatment, the multilayer desorbs from the surface leaving a film similar, in thickness and molecular orientation, to the low coverage situation.

It has to be noted that the angles obtained by NEXAFS might be due to the superposition of two or more orientations. Thus, we rather refer to the molecular orientation α as the "average angle" of the molecule. Moreover, it is important to remind that the obtained angular values are qualitative, since more data points would be needed for a more accurate estimation of the molecular orientation. However, what is clearly shown by our experimental results is that biphenylene molecules show a change in orientation determined by the film thickness. For the low coverage, the molecules mostly lay flat on the surface and for very high coverage, the molecules mainly stand on the surface, probably in a complex arrangement. For the intermediate coverage either the molecules gradually switch from the low coverage to the high coverage arrangement or are on average disposed at an angle α of about 55°. These results confirm that, for the low coverage, molecule-substrate interactions play a sufficiently important role to determine an ordered arrangement of the molecules on the surface. For the high coverage, instead, the molecule-molecule interactions get more importance.

V. CONCLUSIONS

To the best of our knowledge, this is the first characterization of biphenylene deposited on a surface. The analysis of core and valence occupied and unoccupied levels revealed that the adsorbed biphenylene film is characterized by important intermolecular interactions, as can be deduced from the overall broadening of the spectral features when compared with the results of the gas phase measurements and of the single molecule DFT calculations. However, the overall agreement among the thick film, gas phase, and theoretical spectra indicates that biphenylene preserves its molecular character when deposited on Cu(111).

NEXAFS measurements performed on biphenylene adsorbed at different coverages show that the molecular arrangement changes with the film coverage. For very thin and for very thick films, molecules are lying or standing on the surface, respectively. For the intermediate coverage, either the molecules progressively vary their orientation from the low coverage to the high coverage configuration or choose the in-between angle of 55° (the magic angle).

We can conclude that the interaction between the biphenylene and Cu(111) substrate is sufficiently important to
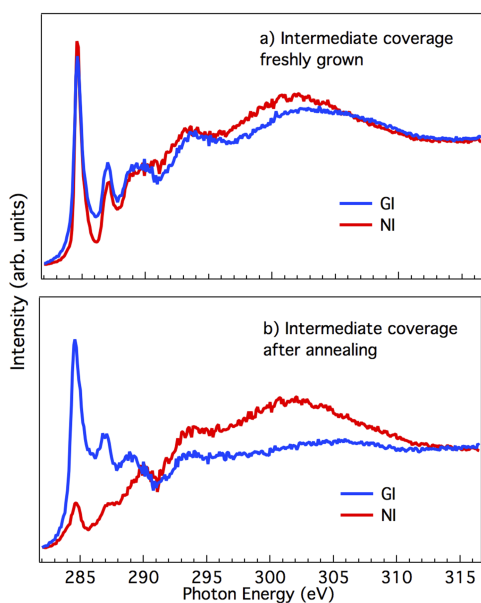

FIG. 6. (a) NEXAFS spectra on a freshly grown film of biphenylene for an intermediate coverage; (b) NEXAFS spectra after the annealing. The acquisition geometries are GI and NI, already used for the low coverage film (see Figure 5).

determine an asymmetric line shape, the disappearance of a shake-up intensity in C 1s PE peak, and a flat lying molecular adsorption for the low coverage biphenylene films.

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