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Adenine adlayers on Cu(111): XPS and NEXAFS study

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The adsorption of adenine on Cu(111) was studied by photoelectron and near edge x-ray absorption fine structure spectroscopy. Disordered molecular films were deposited by means of physical vapor deposition on the substrate at room temperature. Adenine chemisorbs on the Cu(111) surface with strong rehybridization of the molecular orbitals and the Cu 3d states. Annealing at 150 °C caused the desorption of weakly bonded molecules accompanied by formation of a short-range ordered molecular adlayer. The interface is characterized by the formation of new states in the valence band at 1.5, 7, and 9 eV. The present work complements and refines existing knowledge of adenine interaction with this surface. The coverage is not the main parameter that defines the adenine geometry and adsorption properties on Cu(111). Excess thermal energy can further rearrange the molecular adlayer and, independent of the initial coverage, the flat lying stable molecular adlayer is formed. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4935055]

INTRODUCTION

The interfaces formed between fundamental biomolecules and metal surfaces have been a widely studied topic for several decades. The motivation for continued investigation of bio/inorganic interfaces comes mainly from the fast development of organic electronics using biocomponents, biosensors, and drug delivery systems.[1–3] The desire for a better understanding of the interaction of complex biomolecules (DNA, proteins, etc.) with inorganic surfaces has stimulated numerous model studies of simplified systems, one of which is adenine on copper surfaces.

Sub-monolayer coverages of adenine spontaneously form one dimensional molecular chains with rings parallel to the Cu(111) surface, as observed by scanning tunneling microscopy.[4,5] Spontaneous self-assembly was explained by anisotropic intermolecular hydrogen bonding which dominated compared to molecular interaction with the Cu(111) surface.[4] Density functional theory (DFT) computations predicted that adenine lies nearly flat on Cu(111) and interacts weakly with the surface through physisorption,[6] so that adenine does not chemisorb on the (111) surface of copper.

A closely related model substrate is the Cu(110) surface. At coverages of 0.2 monolayer (ML), adenine adsorbs parallel to the Cu(110) surface.[7] The complexity of adenine bonding to Cu(110) was investigated in detail by Feyer *et al.*[8] On the basis of X-ray photoelectron spectroscopy (XPS), near edge X-ray absorption fine structure spectroscopy (NEXAFS) and DFT calculations two bonding mechanisms of adenine on Cu(110) were observed. At 0.18 ML coverage, the molecule interacts via the N7 imino atom (Fig. 1) and partially via the NH_2 amino group, lying flat on the surface. At higher coverage, adenine on Cu(110) undergoes a phase transition driven by the gain in the adsorption energy with significant change of the molecular orientation. The molecule bonded edge-on via the N1 imino atom and to a lesser extent via the NH_2 amino group at 0.3 ML coverage.[8] The existence of two different chemisorbed phases of adenine on Cu(110) depending on coverage was confirmed by ultraviolet photoelectron spectroscopy and reflection high energy electron diffraction.[9] Moreover, a flat-lying ordered phase was obtained by annealing of the multilayer film on Cu(110) at 150 °C.[9,10] The transition from edge-on to flat-lying configuration during annealing was shown to be similar to that obtained in the early stages of molecular growth at room temperature (RT).[9] It was suggested, without direct experimental evidence, that this similarity of flat-lying phases (low coverage deposited at RT and annealed multilayer) is related to thermally stimulated adenine desorption.

The interaction of adenine with noble metals such as gold[11] and silver[12] is weak, with molecules oriented parallel, or at a small angle, to the surface. Adenine adsorption on polycrystalline gold, Au(111) and Au(100) electrodes in aqueous solutions was investigated by cyclic voltammetry and IR spectroscopy.[13,14] The molecule coordinates to the gold substrate via the NH_2 group and N7 ring atom independent of the surface orientation. An electrochemical STM study of adenine on Au(111) has shown the formation of small molecular domains aligned along the three crystallographic surface directions. The chains of molecules are stabilized by π stacking and this yields an adlayer with short-range order.[15] Interaction of adenine with silver nanoparticles or silver roughened electrodes takes place through the amino group NH_2 and N7 ring atom, while bonding to vacuum

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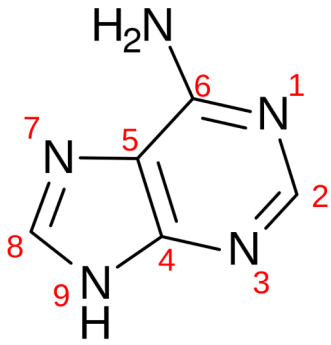

FIG. 1. Schematic structure of adenine ($C_5H_5N_5$).

deposited films was solely via the N7 atom.[16] A unique feature of DNA immobilization via adenine nucleotides on polycrystalline gold surfaces was revealed by FTIR and XPS analysis.[17] It was shown that the adsorption of the adenine nucleotides on gold was much stronger than for the other oligonucleotides (thymine, guanine, or cytosine nucleotides).[18] Attachment of *single-stranded* DNA to gold surfaces via adenine nucleotide blocks[17,18] has a number of potential advantages over using a thiol linker.[19] A recent study of RNA mononucleotides' interaction with silver nanoparticles has confirmed the bonding through the nucleobases, with the ribose tail oriented outwards. The adsorption of adenosine monophosphate on silver nanoparticles was shown to be concentration dependent: at high concentrations, bonding via the N1 atom was favored, and at low concentration, it was via the N1 and the amino group, with the molecular plane close to parallel to the metal surface.[12]

We report here a spectroscopic study of the thermally induced short range adenine ordering on the Cu(111) surface. To our knowledge, no detailed spectroscopic study has been reported on the adenine/Cu(111) model system. The similarity with the Cu(110) surface allows one to suggest that the flat lying adenine phase formation is independent of surface orientation and is a general feature for copper substrates. By ellipsometry, adenine was found to form a thin passivation film on a polycrystalline copper substrate in a hydrocarbon medium, which has protective properties with regard to copper corrosion.[20] Simple thermal treatment at about 150 °C to prepare a saturated adenine film strongly bonded to copper could contribute to the development of novel corrosion protection technologies.

EXPERIMENTAL

The experiments were performed at the Materials Science Beamline, Elettra Sincrotrone Trieste, Italy. The experimental station with a base pressure of 2×10^{-10} mbar is equipped with a Specs Phoibos 150 hemispherical electron energy analyzer, low energy electron diffraction (LEED) optics, a dual-anode Mg/Al X-ray source, an ion gun, and a sample manipulator with K-type thermocouple attached to the rear side of the sample.

The Cu(111) crystal (MaTecK GmbH, 8 mm diameter, 2 mm thickness, 99.999%) was cleaned by several cycles of Ar ion sputtering and annealing to 450 °C. The surface cleanliness was checked by monitoring the C 1s photoelectron signal. No impurities were detected on the Cu(111) surface, which showed a sharp (1×1) LEED pattern before the adenine deposition.

Adenine (99% purity) was supplied by Alfa Aesar and used without further purification. Adsorption of adenine took place in the preparation chamber (base pressure 5×10^{-9} mbar) using a Knudsen-cell type evaporator. Before the deposition, the adenine powder was degassed in vacuum at 110 °C and then heated to 130 °C for the deposition on Cu(111). The deposition rate was about 1 ML per 90 s, determined from the analysis of the photoemission data.

The C 1s and N 1s core levels were acquired with photon energy 410/475 eV and total resolution 420/510 meV, respectively. Valence band (VB) spectra were acquired with photon energy 43 eV and resolution 160 meV. All binding energies were calibrated by measuring the Fermi edge. The intensity of the photoelectron spectra measured with synchrotron radiation was normalized to the incident photon flux. Al K_α radiation (1486.6 eV) was used to measure the core levels of C 1s, N 1s, and Cu $2p_{3/2}$, with total resolution of 1 eV. The emission angle for the photoelectrons was 0° with respect to the sample normal for synchrotron light and 20° for the X-ray source. The incidence angle of the synchrotron radiation at normal emission geometry was 60°. Checks for radiation damage were performed by monitoring the C 1s core level spectra. No spectral changes were observed during one experimental step (about 30 min). The analysis point on the sample surface was changed for each experimental step as a precaution to avoid radiation damage. The homogeneity of the C 1s signal was checked after adenine deposition.

The NEXAFS spectra were taken at the C and N K-edges using the carbon and nitrogen KVV Auger yields, at normal (NI, 90°) and grazing (GI, 10°) incidence of the photon beam with respect to the Cu(111) surface. The energy resolution for the C and N K-edge NEXAFS spectra was estimated to be 230 and 380 meV, respectively. The polarisation of light from the beamline has not been measured but is believed to be 90% linear, as the source is a bending magnet. The raw NEXAFS spectra were normalized to the intensity of the photon beam.[21] Then, the corresponding background spectra of the clean sample recorded under identical conditions were subtracted.

The coverage of adenine was estimated using the parameterized inelastic mean free path λ_m for organic materials,[22]

$$\lambda_m = 49/E_k^2 + 0.11E_k^{1/2}\ \mathrm{mg/m^2}, \quad (1)$$

where E_k is the kinetic energy of photoelectrons. The λ_m value was converted to distances by dividing by the density of adenine powder[23] (1.6×10^9 mg/m^3). The inelastic mean free path for Cu $2p_{3/2}$ photoelectrons (excited by 1486.6 eV photons) passing through the adenine adlayer was found to be 16.2 Å. Using this value, the effective thickness of adenine on different substrates was calculated from the equation

$$I_d = I_0 \exp(-\lambda_m/d), \quad (2)$$

where I_d and I_0 are the attenuated and clean surface intensity of the photoelectron signal and d is the thickness of the

molecular adlayer. The effective thickness d is calculated within a continuum model of the molecular film and it has only qualitative character.

RESULTS

We investigated two different adenine adlayers on Cu(111): 1.6 ML and 0.4 ML. In both cases, adenine was evaporated onto a substrate that was at a temperature of 25 °C and then its thermal stability and bonding geometry were investigated after annealing for 1 min at temperatures 75, 100, 125, 150, 200, and 250 °C. The Cu $2p_{3/2}$ core level was used to determine the effective molecular thickness by measuring the attenuation of the signal after deposition. The values of the thickness were calculated using Equations (1) and (2) and are presented in Table I. 1 ML coverage was defined as saturation coverage, achieved by deposition of a multilayer on the surface and subsequent annealing at 100 °C for 1 min to desorb the weakly bonded molecular species. We estimated the thickness of 1 ML as 3.8 Å, which is a reasonable value considering the size of adenine and in good agreement with the published values.[6,9] The thickness for the submonolayer coverage of 0.4 ML was found by analyzing the C 1s and N 1s core level signals using the corresponding intensities for 1 ML coverage as a reference. For the 0.4 ML adenine coverage, the effective adlayer thickness decreases from 1.6 Å to 0.9 Å after annealing at 100 °C and then remains the same at 250 °C. The similar value of 0.8 Å was reached after final annealing of 1.6 ML sample at 250 °C. This points to molecular desorption and/or a change in the orientation of the adenine molecule on the Cu(111) surface and will be discussed further below.

TABLE I. Thickness of adenine adlayers on Cu(111) as a function of temperature. Binding energies of C 1s and N 1s core level components compared with published data.

	25 °C	100 °C	250 °C
	Adenine adlayer thickness (Å)		
1.6 ML	6.2	3.8	0.8
0.4 ML	1.6	0.9	0.9
	Binding energy (eV)		
C 1s	287.0 (A)	286.7 (A)	...
1.6 ML	286.0 (B)	285.8 (B)	285.8 (B)
	285.2 (C)	284.9 (C)	284.9 (C)
C 1s	286.8 (A)	286.8 (A)	...
0.4 ML	285.8 (B)	285.8 (B)	285.8 (B)
	284.9 (C)	284.9 (C)	284.9 (C)
C 1s	287.4		
0.7 ML adenine/SiO_2[24]	286.7		
	285.6		
C 1s	286.7		
0.18 ML adenine/Cu(110)	285.8		
0.3 ML adenine/Cu(110)[8]	284.9		
N 1s	401.0 (D)	400.0 (D)	...
1.6 ML	399.8 (E)	398.5 (E)	398.7 (E)
	...	...	397.2 (F)
N 1s	399.8 (D)	399.8 (D)	...
0.4 ML	398.5 (E)	398.5 (E)	398.8 (E)
	...	...	397.2 (F)
N 1s	400.7		
0.7 ML adenine/SiO_2[24]	399.7		
	399.5		
N 1s	398.8		
0.18 ML adenine/Cu(110)[8]			
N 1s	398.45		
0.3 ML adenine/Cu(110)[8]	399.8		

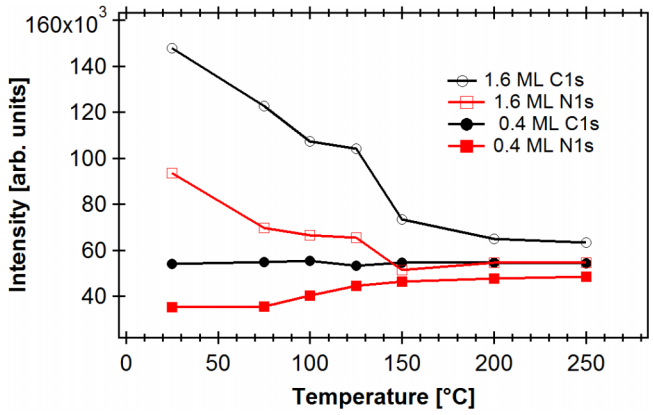

FIG. 2. Intensity of C 1s and N 1s core levels of adenine on Cu(111) versus annealing temperature.

Figure 2 shows the total areas of the C 1s and N 1s core level peaks for both samples depending on the temperature of annealing. The data in the Figure 2 are normalized to the corresponding photoionization cross sections (0.44 Mb for C 1s and 0.49 Mb for N 1s[25]). Two different behaviors are observed. For the 1.6 ML sample, both intensities first decrease, reach a plateau between 100 and 125 °C (defined as 1 ML), and then decrease again and remain almost unchanged starting from 150 °C. In the case of the 0.4 ML sample, the intensity of C 1s is constant at all temperatures and is accompanied by a small increase of the N 1s signal up to 125 °C. Independent of the adenine coverage, the N 1s intensity was found to be lower than C 1s, and the difference is more pronounced for the low temperature region.

The C 1s, N 1s core level, and valence band spectra of 1.6 ML ((a)–(c)) and 0.4 ML ((d)–(f)) of adenine adsorbed on Cu(111) are shown in Figure 3 measured after treatment at different temperatures. The C 1s peak for as-deposited adenine adlayers consists of three clear components A, B, and C independent of initial molecular coverage. They were assigned to different carbon atoms of the adenine molecule: A to C6, B to C2, C4, C8, and C to C5.[26,27] The binding energies of the C 1s components are collected in Table I together with the data on related systems. For the 1.6 ML coverage, the C 1s core level gradually shifts to lower binding energy by 0.4 eV after annealing at 75 and 100 °C. The shift of the spectra was attributed to the change in the core hole screening for lower molecular coverage. Further thermal treatment does not affect the peak position; moreover, the C 1s spectral shape becomes very similar to that of the submonolayer coverage of 0.4 ML. Recalling the intensity curves in Figure 2, the similarity of the C 1s spectra for the two samples indicates the desorption of adenine molecules in the case of 1.6 ML coverage. The

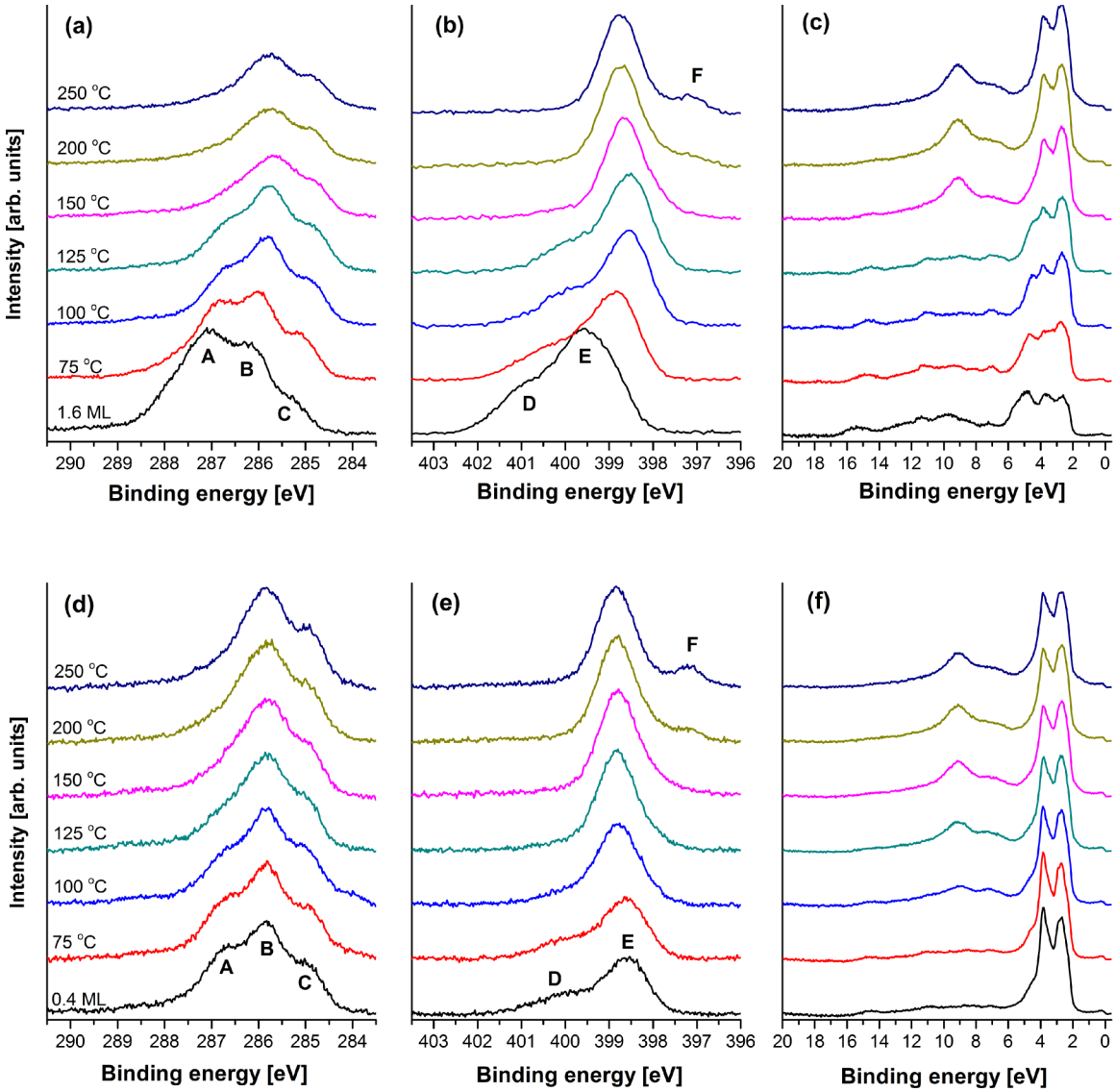

FIG. 3. Photoemission spectra of 1.6 ML ((a)–(c)) and 0.4 ML ((d)–(f)) adenine on Cu(111) acquired at each experimental step: C 1s core level ((a) and (d)), photon energy 410 eV; N 1s core level ((b) and (e)), photon energy 475 eV; and valence band spectra ((c) and (f)), photon energy 43 eV. Light incident at 60°.

shape with three components (A, B, C) of the C 1s core level remains unchanged till 125 °C for 1.6 ML and 100 °C for 0.4 ML adenine adlayer on Cu(111). Thermal treatment at higher temperature causes a decrease of the intensity of the component A at 286.8 eV binding energy. As this component is assigned mainly to C6, we expect a change in the bonding of the molecule to Cu(111) via the amino group.

Similar behavior was observed for the N 1s core level, in which two components D and E are clearly visible after adenine deposition: the shift to low binding energy by 1.0 eV is accompanied by a decrease of the intensity for the 1.6 ML sample after 100 °C annealing. It is worth underlining that the shift of 1 eV for N 1s is much higher than the one for C 1s, which indicates a major change of the nitrogen atom electronic environment on interface formation with Cu(111). The components D and E were attributed initially to amino and imino nitrogen atoms, and their binding energies are collected in Table I. As their intensity ratio D:E did not reach the expected stoichiometric value of 2:3, another point should be taken into account, i.e., the hydrogen bonding contribution, which shifts the energy of amino nitrogen to lower values.[8] Deprotonation also has to be considered as a possible reason for a much lower binding energy of the amino nitrogen component. The component D was assigned to the N9 atom in the closely related system, adenine on Cu(110), supported by theoretical calculations.[8] We use this identification also for our case. The component D gradually vanishes with temperature increase. Two possible reasons can account for this change: thermally activated N9 deprotonation or intermolecular hydrogen bonding[4] which accompanied the adsorption geometry change.

After annealing the 1.6 ML at 125 °C and 0.4 ML at 100 °C, the single component E dominates the N 1s spectrum. Another interesting feature is the shift of the component E to higher binding energy by 0.2 eV in the course of the thermal treatment starting from 100 °C, independent of initial coverage. This is clearly visible for the 0.4 ML sample where no desorption of molecules is observed. As the component

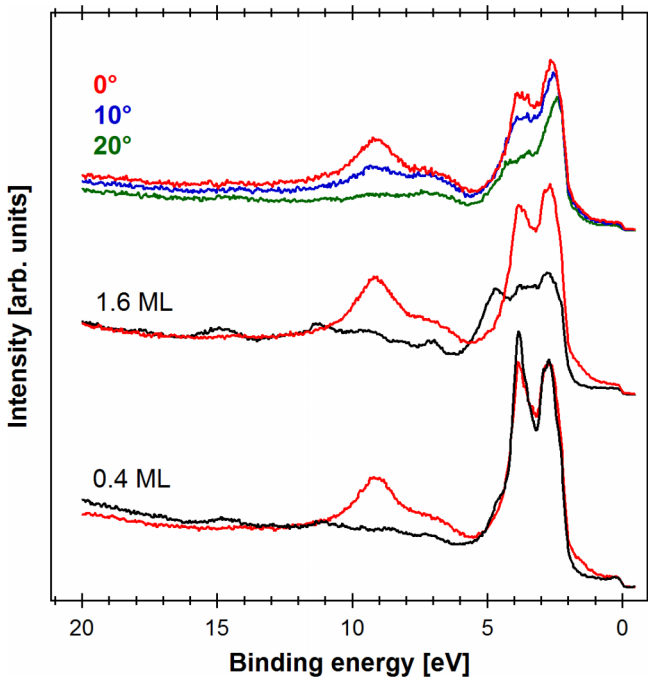

FIG. 4. Valence band spectra, photon energy 43 eV. The spectra at adenine coverage 0.4 and 1.6 ML on Cu(111) after annealing at 75 °C (black line) and 250 °C (red line) are shown. Upper curves: spectra of 1.6 ML adenine on Cu(111) after 150 °C treatment measured at the emission angles shown. Light incident at 60° for 0°(normal) emission and 50° and 40° for 10° and 20° emissions.

E accounts for nitrogen atoms in molecules with more than one bonding configuration, the shift by 0.2 eV points to a change in nitrogen atoms bonding to the surface and/or charge exchange between molecules and the Cu(111) surface. The component F at 397.0 eV appears in the N 1s core level after the treatment at 200 °C and was assigned to the N—Cu direct bond formation.[21] The shift of component E to high binding energy without appearance of the component F proves the formation of a strong bond between adenine and Cu(111), which is different from direct N—Cu bonding.

In Figures 3(c) and 3(f), the VB spectra are shown for both samples. For low adenine coverage (0.4 ML), the original valence band of Cu(111) changes negligibly after deposition mainly because of the low coverage and low photoionization cross section of the molecular orbitals. The adenine orbitals are much more pronounced in the case of the 1.6 ML sample, and the prominent wide feature at about 5 eV is assigned to orbitals with mixed π-σ character.[28] The peak shift of 0.3 eV on the first annealing of the 1.6 ML sample is in line with changes of the core levels due to improved hole screening. The features at 7 and 9 eV were assigned to 18a(π_2) and 16a, 17a(σ) orbitals, respectively, for the free adenine molecule.[28] With increasing temperature, they become more pronounced, independent of the initial coverage. This is well illustrated in Figure 4, comparing the VB spectra after 75 and 250 °C annealing of 0.4 and 1.6 ML adenine coverages. Moreover, the appearance of these peaks happens at the same temperature at which the component A(C6) in C 1s becomes less visible and the component D in N 1s disappears. To explore the origin of the new VB features, the spectra were measured at 0°, 10°, and 20° emission geometry for the 1.6 ML of adenine annealed at 150 °C (see upper panel of Figure 4). We observe that the intensity of the peak at 9 eV strongly depends on the emission angle, i.e., an enhancement of the intensity of the molecular orbitals at normal emission. This suggests that photoelectron diffraction plays a role in determining the intensity of the valence band peaks, as this can give rise to rapid changes of intensity as a function of angle.[29] Furthermore, it implies that the molecules are not only oriented but also locally ordered, since this is a requirement for the effect to occur. While this effect may play a role, we believe that the main cause of intensity enhancement is chemical.

According to Ref. 9, the highest occupied interface states for adenine on Cu(110) lie between 2 and 3.5 eV binding energies, overlapping the Cu 3d states. In our spectra, we cannot judge well the changes in this energy region, but the intensity increases at about 1.5 eV binding energy, which is clearly visible in the VB spectra of adenine on Cu(111) after annealing at 250 °C. This feature appeared as a result of thermal treatment and it is not present in the spectra after annealing at 75 °C. The intensity of this shoulder is higher for the 1.6 ML sample, where the molecular coverage is slightly higher (see Fig. 2).

Figure 5 shows N and C K-edge NEXAFS spectra of 1.6 ML (higher panel) and 0.4 ML (lower panel) adenine on Cu(111) measured in NI and GI geometries after annealing at different temperatures. Sharp peaks at lower photon energies for both N (I, II peaks) and C (V peak) K-edges are due to core level transitions to empty states of π^* symmetry, and the broad peaks (III, IV, VI, VII, VIII) to states of σ^* symmetry. The peak I at 399.5 eV for 1.6 ML coverage was assigned to transitions of 1s electrons from all nitrogen atoms N1, N3, N6, N7, and

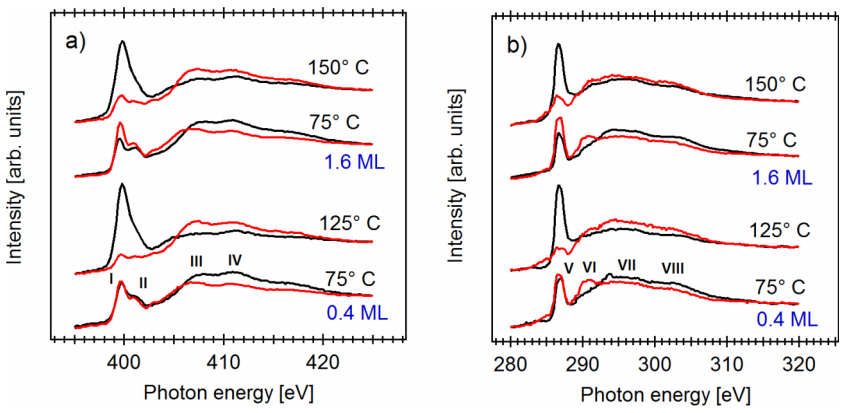

FIG. 5. NEXAFS spectra of adenine on Cu(111): (a) C K-edge, (b) N K-edge. Black line—GI, red line—NI.

N9 to empty antibonding π^* orbitals above the band gap. Its position agrees well with the published values for adenine in the liquid phase[30] (399.5 eV) or thin powder film[31] (399.4 eV). The component II at about 401.0 eV of the N K-edge spectrum was assigned to transitions to the highest unoccupied molecular orbitals of π^* character.[30,31] The peak I shifts by 0.3 eV to high energy after annealing at 150 °C of the 1.6 ML adenine on Cu(111). The same value of 399.8 eV was obtained for the 0.4 ML sample after 75 and 125 °C treatment, which is in agreement with the previously mentioned molecular desorption and with data (400.0 eV) for submonolayer adenine coverage on Cu(110).[8] The π^* resonance range of the C K-edge is dominated by one unresolved component V centered at 286.7 eV photon energy independent of coverage and treatment. For adenine powder, attributed to C═C bonds (286.7 eV) and C—N bonds (287.4 eV),[30] there are two well resolved components at photon energies 286.7 and 287.4 eV. Moreover in our case, it is not a question of insufficient energy resolution because on multilayer thick adenine films, we do resolve the two components of the π^* resonances (data not shown here). The shift of the high photon energy component to lower value, resulting in unresolved π^* resonances peak, confirms that adenine bonds to Cu(111) via the nitrogen atoms. A similar unresolved π^* resonance structure was observed in the O K-edge spectra of the thiolated thymine homo oligonucleotides on Au(111) and was explained by the formation of a specific H-bonded configuration involving the oxygen atoms.[19] The NEXAFS spectra measured at different geometries are very similar after treatment at 75 °C independent of the initial molecular coverage. Annealing at higher temperature (150 °C for 1.6 ML and 125 °C for 0.4 ML) induces a strong angular dependence of the π^*/σ^* intensity ratio. The π^* resonances almost vanish for NI geometry, indicating that the molecular plane is lying flat on the surface.

DISCUSSION

Summarizing all the data, we conclude that adenine molecules form a disordered adlayer during deposition on Cu(111) at room temperature as the absorption spectra do not show any dependence on the incidence angle of photons. Annealing at 75 °C does not influence the molecular orientation on the surface much (Fig. 5); the main change is the drop in C 1s and N 1s intensities for the multilayer film (Fig. 2). The desorption of molecules is responsible for the intensity decrease during thermal treatment of 1.6 ML of adenine on Cu(111), which is quantified by the effective adlayer thickness value change (Table I). The occurrence of desorption was supported by the strong reduction of the adenine molecular sticking coefficient on Cu(110) above 100 °C.[10] Independent of the initial coverage, almost the same value of the effective thickness was reached after 250 °C annealing (Table I), which is in line with the oriented molecular adlayer formation deduced from the NEXAFS data. For the sub-monolayer phase of adenine on Cu(111), only an improvement of the ordering was observed for the same treatment, without molecular desorption (Figs. 2 and 5). Apart from the attenuation of the (1×1) clean surface pattern, no additional superstructure was observed by LEED for any adenine adlayer on Cu(111).

Since there are equal numbers of carbon (5) and nitrogen (5) atoms in the adenine molecule, and the photon flux and the analyzer transmission are similar for these core levels, the C 1s and N 1s intensities are expected to be comparable, as in fact was observed for samples treated above 150 °C. The lower intensity for the N 1s level was attributed to a characteristic interface between the adenine and the copper surface. The kinetic energy of the photoelectrons was 125 eV and 75 eV for C 1s and N 1s, respectively, corresponding to extremely surface sensitive conditions. Most likely, the N 1s signal was attenuated more than C 1s because of disordered adlayer formation after adenine deposition, and bonding at the interface via nitrogen atoms. As the thermal treatment promotes flat-lying adenine orientation on Cu(111) (Fig. 5), where the molecule is almost parallel to the surface, the intensity values for C 1s and N 1s become similar, i.e., no significant attenuation of any signal is observed.

The C 1s and N 1s photoelectron spectra for high (1.6 ML) and low (0.4 ML) adenine coverage on Cu(111) differ in binding energy values of the components and their ratio. For both cases, the evolution of the spectra with thermal treatment is similar, but the changes occur earlier on the temperature scale for 0.4 ML, as there are less molecules on the surface. The annealing at 100 °C of the 1.6 ML adlayer gave the same C 1s and N 1s spectral shape and peak position as those of 0.4 ML adenine on Cu(111) (Fig. 3 and Table I). As the N 1s core level is more affected on thermal treatment than C 1s, we expect that the main contribution to interface formation is from nitrogen rather than carbon derived orbitals, as reported also for Cu(110) surface.[7,8] The absence of the component F (see Figures 3(b) and 3(e)) for the lower temperatures is another indirect proof that the adenine molecule on Cu(111) is integral with protonated nitrogen atoms involved in the hydrogen bond network or interface formation with Cu(111). The stoichiometry of the adenine molecules after evaporation in vacuum and adsorption on Cu(111) was cross checked by forming a multilayer molecular film (data not shown here) using the C 1s and N 1s signals measured with 1486.6 eV photon energy. The ratio of peak intensity C:N divided by the corresponding photoionization cross sections[25] was found to be 1:(1.09 ± 0.10), in good agreement with the expected value 1:1.

The information provided by the analysis of the present photoemission data is insufficient to define precisely which nitrogen atom binds the molecule to the surface. Bearing in mind the similarity of our spectra to those published by Feyer *et al.* for adenine on Cu(110),[8] we suggest the same nitrogen atom involvement for the flat adsorption geometry. For molecules almost parallel to the surface, the interface is formed via N7 and partially via the amino N6 atom.[8] Differently from the cited work, we suggest that the saturated coverage of adenine on Cu(111) reached after 100 °C is a mixed disordered phase consisting of different bonding geometries. Formation of a hydrogen bond intermolecular network is responsible for the single component of the N 1s peak. The vanishing of the A(C6) component at 150 °C for 1.6 ML and 125 °C for 0.4 ML indicates that there is probably a change in amino group bonding to the surface or participation in hydrogen bonding. At temperatures 200 °C and

higher direct bonding between N and Cu atoms was observed (N 1s component F) indicating deprotonation of some of the amino nitrogen atoms.

The flat molecular geometry promotes the rehybridization between π orbitals of adenine and d orbitals of copper accompanied by electron exchange. This electron exchange is represented by the N 1s spectra shifting to higher BE by 0.2 eV, observed also by Feyer *et al.* for adenine on Cu(110), with unchanged C 1s core level and with the appearance of a small shoulder in the VB spectra at 1.5 eV. The lack of C 1s shift again confirms that only nitrogen atoms are involved in the interface formation. The intensity of the VB shoulder at 1.5 eV increases gradually with temperature so we can exclude direct bonding between N and Cu as a possible reason for this feature.

Parallel orientation of the adenine plane with respect to the surface, in which the π orbitals are perpendicular to the surface, is expected to enhance the photoelectron signal from π orbitals at normal emission geometry of photoelectron collection.[9] Independently of the previous assignment according to Ref. 28, we conclude that the features at 7 and 9 eV in the VB spectra are the interface states of adenine/Cu(111) system which have mainly π character, confirming the flat lying molecular orientation on Cu(111) after 150 °C annealing. The state at 1.5 eV was observed also for a flat lying adenine adlayer on a Cu(110) surface.[9] Thus, the strong interaction of adenine with the copper surface accompanied by improved parallel ordering is thermally induced through rehybridization of the adenine π and copper 3d orbitals and charge redistribution between them. This is in line with the N 1s core level shift by 0.2 eV and unchanged position of C 1s, which confirm mainly nitrogen orbital involvement in the interface formation.

We would like to address the definition of the saturation coverage of molecules on the surface. For a monolayer prepared by thermal treatment of multilayer films, the question arises about how high the temperature of annealing has to be. Obviously, the exact value of temperature is found empirically and defines the molecular adlayer stability in a certain temperature range, i.e., where the interface electronic structure and adsorption geometry are conserved. In the present work, we define ML as the saturation coverage after annealing of the multilayer film at 100 °C characterized by disordered adlayer formation, which remains unchanged after 125 °C treatment and starting from 150 °C the ordered phase of flat lying adenine on Cu(111) is formed. For the 0.4 ML sample, the temperature of surface reordering is 125 °C. Thus, the exact temperature depends also on the initial molecular coverage. Relative to the published work on the saturation coverage of adenine[8] (guanine[32]) on Cu(110) reached by flashing the multilayer to 160 °C (230 °C) where a coverage of 0.3 ML was reported, our oriented adlayer should be taken as 0.3 ML in their units. In the cited papers, the coverage was calibrated by reference to CO and O_2 adlayers analyzed using Al K_α radiation. Here, we estimated the coverage from the attenuation of the Cu signal and we obtained the value of 0.4 ML, which is in reasonable agreement with the expected value of 0.3 ML.

The present study together with the published works[8,9] demonstrates that the flat lying adenine adlayer can be easily prepared on the model copper surfaces independent of their orientation.

CONCLUSIONS

The short-range ordered sub-monolayer phase of adenine was prepared on Cu(111) and characterized in detail by spectroscopic techniques. The flat lying molecular adlayer is achieved as a result of thermal treatment of the multilayer as well as sub-monolayer adenine films. The adsorption geometry change is accompanied by desorption of weakly bound molecules. New interface valence band states were observed with strong intensity at normal emission geometry. The strong interaction with Cu(111) keeps the molecule intact on the surface till 200 °C. Bonding to the surface is predicted to be via the N7 imino atom and the amino NH_2 with formation of an intermolecular hydrogen bond network, as for adenine on the Cu(110) surface.[8] Chemisorption of the adenine adlayer on the flat and relatively inert Cu(111) surface was shown. In contrast with the low symmetry Cu(110) surface, only one well defined adsorption phase of adenine on Cu(111) was detected.

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