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Bonding at the organic/metal interface: Adenine to Cu(110)

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The prototypical adsorption system adenine/Cu(110) has been studied by core-level photoemission, x-ray absorption, and *ab initio* calculations. At low coverage, the molecule adsorbs nearly parallel to the surface and bonds by the interaction of one amino and one imino nitrogen atom. At high coverage, the molecular plane is strongly tilted, and the bonding is markedly different. These findings resolve contradictions between calculated adsorbate geometries and published vibrational spectra and illustrate the complexity of the interaction between a relatively simple biomolecule and a metal.

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I. INTRODUCTION

The interaction of organic molecules with surfaces is of great current interest, both from applied (organic electronics, sensors, biocompatibility) and fundamental points of view, and the nature of the chemical bond between surfaces and these molecules has been much discussed.[1–6] Nucleobases represent an important class of biomolecules, and in studies of their adsorption, adenine on Cu has drawn much attention as a prototypical case. On the Cu(111) surface, this molecule self-organizes into chains and networks: a phenomenon which may give insight into the origins of life and have applications in organic device technology.[7] Adenine also forms chains on Cu(110) which are chiral due to the low symmetry of this surface and enantioselective in their interactions with amino acids.[8–10] However, the nature of the bonding of adenine to copper remains controversial, as there is a conflict between experimental[3,8,11,12] and theoretical[2,8,13,14] descriptions of the chemical bond. Vibrational studies[3,8,11] reported very different intensities for the same band (NH_2 scissor mode) and drew conflicting conclusions for the orientation of the molecule. The near-edge x-ray absorption fine structure (NEXAFS) and x-ray photoelectron spectroscopy (XPS) study of Furukawa *et al.*[12] concluded that at low coverage adenine adsorbs parallel to the surface. Theoretical calculations[2,8,13,14] agree in predicting that the molecule is oriented nearly parallel to the surface, but disagree on the strength and nature of the bond, and do not agree with the mechanism proposed by Furukawa *et al.*[12] It is important to reach a consensus on how a fundamental molecule such as adenine—part of the alphabet of life—interacts with a relatively simple surface such as copper, if we are to have confidence in our ability to understand more complex systems. In this paper, we present experimental and theoretical results which resolve this controversy and show that there is not a single bonding mechanism but at least two. Taking this into account, calculations describe accurately both the spectra and the nature of the bond.

The rest of the paper is organized as follows. In Sec. II the experimental and computational methods are described. In Sec. III the relaxed geometries, the C 1*s* and N 1*s* XPS, and N *K*-edge NEXAFS at low and high coverages are discussed. In Sec. IV the paper is summarized.

II. METHODS

A. Experimental setup

The experiments were performed at the Materials Science Beamline, Sincrotrone Trieste, Italy,[15] and the Cu(110) crystal was cleaned by standard sputtering and annealing cycles. Adenine was evaporated in a preparation chamber at a temperature of 400 K, and the coverage was controlled at low coverage by the evaporation time. Saturation coverage was defined as that obtained by adsorbing an excess of adenine and subsequently heating to 430 K to desorb multilayers.[3,8] Care was taken to avoid the radiation damage of the sample. The linearly polarized synchrotron light was incident either at normal incidence (NI) or along an azimuth at approximately 25° to the $[\bar{1}10]$ azimuth. The total resolution was 0.3 eV for NEXAFS taken in nitrogen KVV Auger yield mode and 0.45 eV for photoemission. The coverage was calibrated using XPS with Al $K\alpha$ radiation as the excitation source and by reference to CO and oxygen adlayers. Oxygen forms a $p(2\times1)$ layer of coverage 0.5 monolayer [(ML) one atom or molecule per surface Cu atom]; the O 1*s* signal from this layer was used to calibrate the coverage of CO adsorbed at 140 K (which did not form a well-ordered layer.) The CO coverage was found to be 1.25 ML. From comparison of the C 1*s* signals of CO and adenine, the coverage of adenine at saturation was determined to be 0.3 ± 0.05 ML.

B. Computational methods

Calculations were performed within the density-functional framework using the QUANTUM-ESPRESSO package.[16] The electronic structure is described with the generalized gradient approximation Ref. 17. Ultrasoft pseudopotentials[18] are used and the electronic wave functions and charge density are described by plane-wave basis sets with cutoffs of 30 and 250 Ry. Atomic positions at equi-

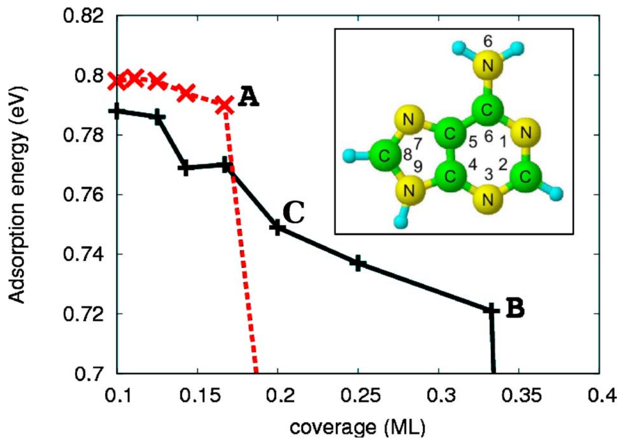

FIG. 1. (Color online) Adsorption energy versus the coverage of adenine on Cu(110) in the parallel (dotted red curve) and perpendicular (full black line) phases. Inset: schematic molecular structure of adenine.

librium were found with the condition that the Hellmann-Feynman forces are <1 meV/bohr. Only the two uppermost copper layers and the adenine molecules were allowed to relax. We considered supercells (SCs) consisting of four atomic layers of copper plus two adenine molecules and a vacuum layer of 10 Å. All surface calculations were performed at the theoretical lattice constant a_0=3.693 Å of fcc Cu, in good agreement with the experimental value a_0^{exp}=3.615 Å. We calculated XPS spectra using the full final-state method.[19] All N 1*s* (C 1*s*) shifts between levels were calculated as differences with respect to the 1*s* level of the N1 (C2) atom (inset, Fig. 1) and then shifted by a constant value determined by aligning the theoretical and the experimental XPS spectra in the low coverage case. Comparison of the calculated and experimental gas phase spectra indicates an accuracy in relative energy of 0.1 eV and 0.26 eV for the N 1*s* and C 1*s* levels, respectively.

Scanning tunnel microscope (STM) measurements at low coverage[8] show the formation of adenine chains along the $[1\bar{1}2]$ and $[1\bar{1}\bar{2}]$ directions on the Cu(110) surface. Therefore, we considered a monoclinic SC defined by the vectors $\mathbf{r}_1=ma_0[\bar{1}10]/\sqrt{2}$, $\mathbf{r}_2=a_0[\bar{1}10]/\sqrt{2}+2a_0[001]$, and $\mathbf{r}_3=8a_0[110]/\sqrt{2}$, where m varied from 2 to 10, in order to calculate the adsorption energy as a function of coverage. When m=6, the monoclinic SC is equivalent to the one derived from low-energy electron diffraction (LEED) and STM measurements by Chen *et al.*[8] and used by Preuss and Bechstedt[13] to study the adsorption energy at low coverage. Converged $4\times4\times1$ and $2\times4\times1$ Monkhorst-Pack meshes for the k-point integrations are used in these monoclinic SCs when $m\leq4$ and $5\leq m\leq10$, respectively. For each supercell, we considered two starting configurations containing two adenine molecules which were allowed to relax.

In the first configuration (parallel geometry), the molecules were initially parallel to the surface so that all imine atoms (N1, N3, and N7) were near one surface upper-layer atom. The experimentally observed $C2$ symmetry[8] was imposed with the symmetry axis passing through an appropriate surface Cu atom, and in such a way that the H9 and N3 atoms form two hydrogen-bonded pairs. Compared to the configurations described by Preuss and Bechstedt,[13] which refer to the m=6 case, this choice yields (after relaxation) a higher adsorption energy of 0.790 eV mainly due to the covalent imino-Cu interaction.[14] This value is 240 meV larger than the adsorption energy found for their D $(5\cdots6)$ geometry.[13] For this particular configuration, our calculated adsorption energy (0.49 eV) is in agreement with their previous result of 0.55 eV.[13]

In the second configuration (perpendicular geometry), the two adenine molecules were initially attached perpendicular to the surface via the N1 imino atom to an upper-layer Cu atom. This corresponds to the lowest-energy configuration found for one isolated adenine molecule. The minimum-energy geometry for the isolated molecule corresponds to a tilt angle of 81.4° and a covalent bond through the N1 imine atom with a bond length of 2.08 Å. The adsorption energy is 0.738 eV, i.e., 398 and 158 meV higher than the values reported in Refs. 2 and 14, respectively. Among the possible starting geometries, we determined the one which maximized the adsorption energy after relaxation.

III. RESULTS AND DISCUSSION

In Fig. 1 we show the calculated adsorption energy per molecule as a function of the coverage for both cases. At low coverage, the parallel configuration is the most favorable up to a coverage of 0.167 ML corresponding to m=6. At higher coverage, the perpendicular case becomes preferred. The calculated adsorption energy per unit of surface (adsorption energy density) increases from 13.7 meV/Å^2 at θ=0.17 ML (point A on Fig. 1) to 15.5 meV/Å^2 at θ=0.2 ML (point C in Fig. 1) when the system undergoes a phase transition. It is reduced to 13.3 meV/Å^2 at θ=0.2 ML if the system is constrained in the parallel phase. The adsorption energy was positive for parallel (perpendicular) configurations and values of m smaller than 5 (3); that is, the adenine chemisorption is stable up to these coverages. Thus, the theory predicts the appearance of two phases: a parallel geometry at low concentration and a perpendicular one at high concentration. The predicted saturation coverage is 0.33 ML corresponding to m=3, and this was confirmed by the measured saturation coverage, which is 0.3±0.05 ML. At this coverage (point B in Fig. 1), the adsorption energy per surface is maximal and equal to 24.9 meV/Å^2.

In Fig. 2 we plot the relaxed geometry at low coverage (point A in Fig. 1) together with the charge-density difference $\Delta\rho$ calculated as in Ref. 2. The adenine molecules are bonded mainly via the N7 imine atoms (bond length $|$N7-Cu$|$=2.11 Å) and less strongly by the N6 amine atoms ($|$N6-Cu$|$=3.16 Å). The adenine plane is tilted by α=28° with respect to the copper surface. Hydrogen bonds between the N3 and N9H amino, as well as between the C8H and N1 atoms, are also observed in the relaxed structure. As mentioned above, low coverages were prepared by evaporation for a short time, and the coverage was 0.18±0.03 ML for the data shown in Fig. 3 upper panel. Figures 3 and 4 compare the experimental XPS spectra with the calculated N 1*s* and C 1*s* core-level shifts of the present relaxed structure Th1.

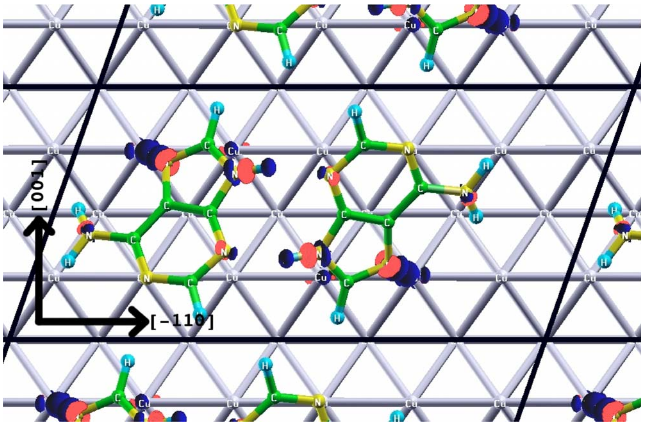

FIG. 2. (Color online) Total charge-density difference for adenine adsorbed in the parallel geometry. Regions of electron accumulation and depletion are in blue (black) and pink (gray), respectively; isosurface value: ±0.008 e/bohr^3. Straight black lines: unit cell proposed by Chen *et al.* (Ref. 8).

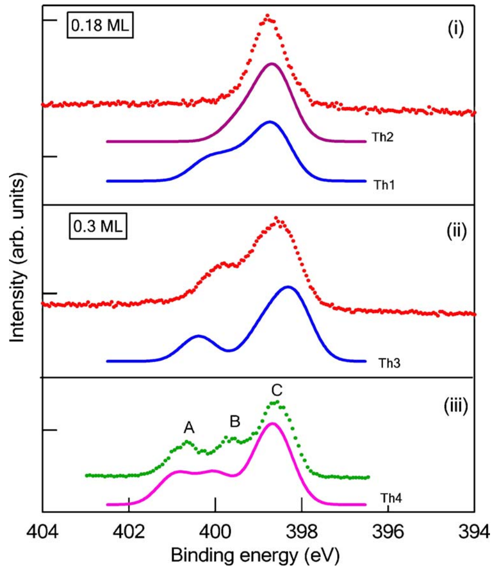

FIG. 3. (Color online) N 1s XPS of adenine/Cu(110) at coverages of (i) 0.18 ML, (ii) 0.3 ML, and (iii) in the gas phase (Ref. 20) shifted −5.3 eV. Peak *A*: emission from N9; *B*: emission from amino NH_2; and *C*: emission from N1, N3, and N7. Points: experimental data; solid lines: calculated spectra. Th1: theoretical spectrum for the geometry shown in Fig. 2. Th2: theoretical spectrum for α=5°. Th3: theoretical spectrum for the geometry in Fig. 6. Th4: theoretical gas phase spectrum. The theoretical lines include a Gaussian broadening with a standard deviation of 0.4 eV and absolute shift of 398.6 eV for Th1 to Th3.

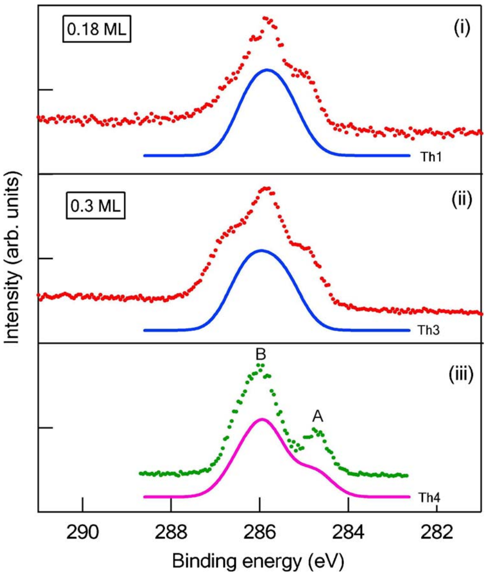

FIG. 4. (Color online) C 1s XPS of adenine/Cu(110) at coverages of (i) 0.18 ML, (ii) 0.3 ML, and (iii) in the gas phase (Ref. 20) shifted −5.7 eV. Peak *A*: emission from C5; *B*: emission from C2, C8, C4, and C6. Points: experimental data; solid lines: calculated spectra. Th1: theoretical spectrum for the geometry shown in Fig. 2. Th3: theoretical spectrum for the geometry in Fig. 6. Th4: theoretical gas phase spectrum. The theoretical lines include a Gaussian broadening with a standard deviation of 0.4 eV and absolute shift of 285.6 eV for Th1 to Th3.

The N 1s experimental spectrum is similar to that of Furukawa *et al.*[12] for 0.2 ML. Taking account of the accuracy of the density-functional theory (DFT) method as judged from the calculation of the gas phase spectrum, 0.1 eV for N 1s and 0.26 eV for C 1s, the theoretical N 1s and C 1s spectra are in reasonable agreement with the experiments. In order to assess the influence of the N9H-N3 hydrogen bonds on the N 1s core-level shifts, we artificially imposed a reduced tilt angle and observed the best agreement with the experimental spectrum for a tilt angle of ≈5°. Such a configuration moves the energy of the N9H core level toward that of the N1, N3, and N7 imine core levels (curve Th2 in Fig. 3), thus reproducing better the experimental single XPS peak. The C 1s spectra are not affected by this geometry change since these modified H bonds do not involve the C atoms. The larger predicted value of 28° for α may be attributed to the poor modeling of the dispersion energy within the DFT scheme.[1,21] In particular, Rauls *et al.*[14] estimated an increase of up to 14% in the adsorption energy of an isolated adenine molecule on the Cu(110) surface if one includes the van der Waals interactions. Nevertheless, we expect in our case a smaller ratio since our relaxed geometry exhibits stronger bonds.

Figure 5 shows the NEXAFS spectra at the same coverage of 0.18 ML. These spectra are also in agreement with those of Furukawa *et al.*[12] and indicate that adenine adsorbs nearly parallel to the surface. Analysis yields an angle between 0° and 27° for the angle between the surface and the molecular plane. The wide error bar arises because the σ region may also contain resonances of π symmetry, and additional surface resonances may be present. Furukawa *et al.* found that the molecular plane was nearly parallel to the surface but did not quantify the angle. These findings are in agreement with our calculations and suggestion that the molecule is close to parallel to the surface due to the hydrogen bonding.

Our calculations predict that for the adenine coverage between θ=0.2 and 0.33 ML, the molecules are adsorbed perpendicularly to the copper surface. The experimental NEX-

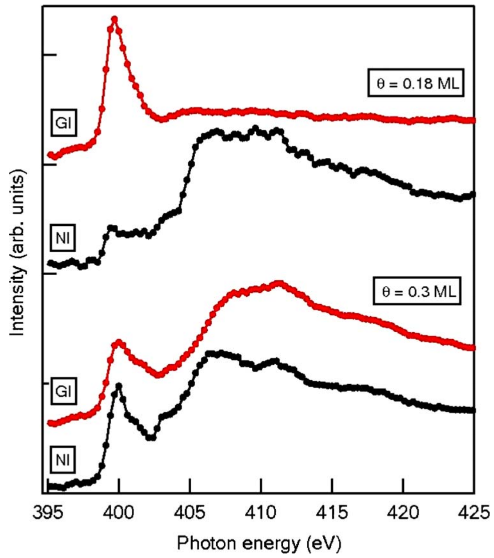

FIG. 5. (Color online) N *K*-edge NEXAFS spectra of adenine adsorbed on Cu (110) and annealed to 430 K and measured at grazing (GI) and normal (NI) incidence of the x rays. The coverage is indicated.

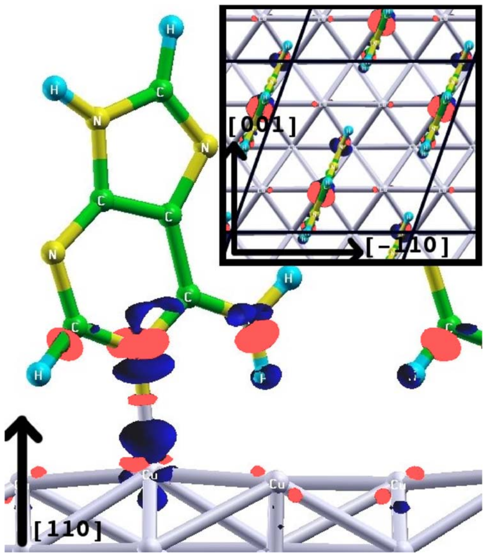

FIG. 6. (Color online) Plot of the total charge-density difference. Regions of electron accumulation and depletion are displayed in blue (black) and pink (gray), respectively; isosurface value: ±0.005 e/bohr^3.

AFS data at the N *K* edge (Fig. 5) show that the angular dependence of the π and σ resonances is reversed with respect to the low coverage situation. This indicates that the molecule is oriented with the molecular plane at a steep angle to the surface greater than 55°. This adsorption geometry is consistent with the vibrational spectroscopy data of McNutt *et al.*[3] and may be the reason that they concluded that the molecule was oriented edge on to the surface. Compared to the low coverage case, both theoretical and experimental N 1*s* and C 1*s* spectra at the high coverage mainly change at high binding energy (Figs. 3 and 4) due to the chemical shift of the N9 (for N 1*s*) and C6 (for C 1*s*) core level. Moreover, the large (small) change of the N 1*s* (C 1*s*) spectra with the coverage reflects the nature of the bonding of the adenine molecules to the Cu surface via the N atoms only (Figs. 2 and 6).

Figure 6 shows the relaxed geometry at the highest theoretical stable concentration (i.e., saturation coverage) 0.33 ML, which has an adsorption energy of 0.721 eV (point *B* in Fig. 1). The adenine molecule is tilted by $\alpha = 89.75°$ with respect to the copper surface to which it is bonded mainly via the N1 imino atom ($|\mathrm{N1\text{-}Cu}| = 2.105$ Å) but also partly via the N6 amino group ($|\mathrm{N6\text{-}Cu}| = 3.31$ Å), as inferred by the total charge-density difference.

The broad field of the bonding of organic molecules to metal surfaces was reviewed by Barlow and Raval,[22] with copper as the most frequently discussed substrate. Very many bonding mechanisms have been observed, depending on the functional groups contained in the molecule. There is a general tendency for large flat molecules to adsorb parallel to the surface at low coverage, particularly if the molecule contains unsaturated ring structures. How the adsorption geometry evolves is then determined by the nature of other functional groups, which are amine and imine groups for adenine, and the relative strength of the interactions. The present study indicates the difficulty of understanding a system which had apparently been well studied by STM, vibrational spectroscopy, and theoretical calculations. Apparent contradictions between these studies have been resolved, in part, by measuring the coverage dependence.

IV. CONCLUSION

In conclusion, the bonding of adenine to Cu(110) can be summarized as follows. At low coverage, the molecule interacts via the N7 imino atom and to a lesser extent via the NH_2 amino group. The hydrogen bonding also shifts the amino core levels toward the binding energy of the imino nitrogen atoms. At high coverage, adenine/Cu(110) undergoes a phase transition driven by the gain in the adsorption energy density and the bonding changes significantly. The molecules are bonded edge on via the N1 imine atom and to a lesser extent also via the NH2 amine. The angular dependence of the NEXAFS spectrum, as well as the N 1*s* core-level spectrum, changes to reflect this reorientation. In contrast to the substantial N 1*s* core-level shifts, the small changes in the C 1*s* spectra with coverage confirm that adenine bonds only via the N atoms to the Cu surface and not via carbon. Compared to the adenine adsorption on the less corrugated Au(111) surface,[23] the bonding is markedly different. On Au, two phases are observed, but in both of them the molecules are nearly parallel to the surface and physisorbed. On Cu(110), chemisorption bonds form and this appears to be the reason for the perpendicular geometry which is not observed on Au.

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