Role of the van der Waals interactions on the bonding mechanism of pyridine on Cu(110) and Ag(110) surface: First-principles study

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We performed density-functional calculations aimed to investigate the adsorption mechanism of a single pyridine (C\(_5\)H\(_5\)N) molecule on Cu(110) and Ag(110) surfaces. Our \textit{ab initio} simulations show that, in the ground state, the pyridine molecule adsorbs with its molecular plane perpendicular to these substrates and is oriented along the [001] direction. In this case, the bonding mechanism involves a \(\sigma\) bond through the lone-pair electrons of the nitrogen atom. When the heterocyclic ring is parallel to the surface, the bonding takes place via \(\pi\)-like molecular orbitals. However, depending on the position of the N atom on the surface, the planar adsorption configuration can relax to a perpendicular geometry. The role of the long-range van der Waals interactions on the adsorption geometries and energies was analyzed in the framework of the semiempirical method proposed by Grimme [J. Comput. Chem. \textbf{27}, 1787 (2006)]. We demonstrate that these dispersion effects are very important for geometry and electronic structure of flat adsorption configurations.

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I. INTRODUCTION

To surpass the intrinsic size limits of the silicon-based electronic devices, the coupling between the molecular and the macroscopic world is at the moment one of the most important perspectives. The ultimate goal of this approach is to construct devices in which the adsorbed organic molecules on surfaces are the main functional units.\(^1\) Among the advantages of using molecules in future electronic devices, it is worth mentioning the possibility of designing such devices at a molecular scale to construct organic field-effect transistors\(^2\)–\(^4\) or ultrahigh-density memory circuits.\(^5\)

A promising way to manufacture a molecular electronic device is to use self-assembled monolayers (SAM)\(^6\) adsorbed on a specific substrate. This approach was employed, for instance, to study several thiolate SAMs on gold surfaces (see, for instance, Refs. 7–9). Single molecules with thiol ends were also used to construct single-atom transistors.\(^10\) To elucidate the electronic structure of certain thiol-based SAM-substrate interfaces, several theoretical studies were performed.\(^11\)–\(^13\) In particular, these \textit{ab initio} simulations clearly emphasized that the electronic properties of a SAM-substrate system depend on a delicate balance between molecule-molecule and molecule-substrate interactions.

Less investigated are systems where the binding atom between the molecules and surfaces is not a sulfur or an oxygen atom (as a part, for instance, of a carboxylate anchoring group\(^14\)–\(^16\)). Therefore, in the present study we focus on the bonding mechanism of a single pyridine molecule adsorbed via its nitrogen atom on Ag(110) and Cu(110) surfaces. Our interest to analyze the behavior of a single molecule is basically motivated by the need to separate the two above-mentioned competing interactions present in a SAM. For a metallic surface, the adsorption process of a single pyridine molecule was investigated from first-principles for Au(111) (Ref. 17) and Cu(100) (Ref. 18) substrates. In particular, the specific nature of the molecule-surface bonding mechanism (physisorption or chemisorption) is the key factor, which largely determines the characteristics of a molecular-based electronic device.

The adsorption process of pyridine (C\(_5\)H\(_5\)N) as a function of temperature and coverage was experimentally studied for several metal surfaces (see, for instance, Ref. 19 and the references cited therein). The peculiar feature of this molecule is the possibility to interact with the substrate: (i) via its planar aromatic \(\pi\)-like molecular orbital in a similar fashion to benzene (C\(_6\)H\(_6\)) on Cu(110) surface\(^20\) or/and (ii) through its nitrogen lone-pair electrons. In the first case the pyridines adsorbs with its molecular plane parallel to surface, while in the second case the heterocyclic ring is perpendicular to surface. At low coverage, the competition between these two adsorption mechanisms might lead to a planar, tilted, or perpendicular binding geometries as well as a mixture of them.

Remarkably, in the case of pyridine on Ag(110) surface a recent low-temperature scanning tunneling microscopy (STM) investigation\(^22\) showed that the isolated molecule binds to this surface only through the nitrogen lone-pair electrons. Similarly, the electron stimulated desorption ion angular distribution (ESDIAD) studies\(^23\)–\(^24\) of the isolated pyridine on Cu(110) surface also revealed a perpendicular adsorption geometry. In these studies it was assumed that the heterocyclic ring is oriented along the [001] direction of the (110) surface. Another possible orientation of the molecular plane is along the [1\(\bar{1}\)0] direction or it can be even twisted between these two directions. However, the STM study\(^19\) of C\(_5\)H\(_5\)N on the Cu(110) surface suggested also the presence of a tilted adsorption geometry in the limit of a very low coverage. In this peculiar case, the adsorption process involves both the nitrogen lone-pair and \(\pi\)-like molecular orbitals.

Since the bulk structure of both metals is face-centered cubic (fcc), an upright binding geometry of pyridine on the (110) surface suggests a similar interaction pattern of this molecule with the substrates under consideration. In this con-
text, it is interesting to analyze how the relative position of
the $d$ band of the Cu(110) and Ag(110) surfaces with respect
to their Fermi level changes the physical properties of the
molecule-substrate interface. Therefore, in the present study
we focused on the bonding mechanism of pyridine on these
surfaces by performing ab initio simulations. To elucidate
the role of the orientation of the molecular plane on the adsorp-
tion process, we considered several adsorption geometries
with the heterocyclic ring parallel or perpendicular to sub-
strates. The relevance of long-range van der Waals interac-
tions on the molecule-surface adsorption process was investi-
gated by means of a semiempirical approach. The total-
energy calculations showed that in the ground-state
adsorption configuration of pyridine on Cu(110) and Ag(110)
surfaces, the heterocyclic ring is indeed perpendicular to
these substrates and oriented along the [001] direction. In
general, the van der Waals interactions are more important
for the parallel adsorption configurations than for the perpen-
dicular ones. From electronic point of view, the binding of
C$_5$H$_5$N on these surfaces is governed by a strong hybridiza-
tion of the highest occupied molecular orbital (HOMO) with
the $d$ band of the substrates. Interestingly, on both substrates
the lowest unoccupied molecular orbital (LUMO) does not participate to the bonding mechanism.

II. THEORETICAL METHOD

To analyze the physical properties of the pyridine-metal
surface interface we performed first-principles total-energy
calculations based on the density-functional theory (DFT)
(Ref. 25) in a pseudopotential plane-wave implementation as
provided by the VASP code. The electron-ion interactions
were taken into account by pseudopotentials generated using
the projector augmented wave (PAW) method. For the ex-
change-correlation energy functional we employed the
generalized gradient approximation (GGA) as parameterized
by Perdew et al. [Perdew Burke Ernzerhof (PBE) energy
functional].

The molecule-metal system was modeled by a repeated
slab consisting of five atomic layers separated by a vacuum
region of $\approx 16$ Å. We checked the consistency of our results
by using seven and nine atomic layers, respectively. A single
pyridine molecule was adsorbed on one side of the slab. To
avoid the interactions between a molecule and its peri-
codically repeated images, a $4 \times 5$ in-plane surface unit cell for
the Cu(110) and Ag(110) surfaces was utilized. The (110)
surfaces of these metals were generated using the theoretical
lattice parameters calculated for the bulk copper (3.636 Å)
and silver (4.165 Å), respectively. The geometry of the
pyridine-(110) metal surface was optimized by relaxing all
molecule atoms and those of the two surface layers. The
 corresponding relaxed geometries were obtained when the
calculated Hellmann-Feynman forces were smaller than
$\approx 0.001$ eV/Å. To calculate such accurate forces, the plane-
wave basis set included all plane waves up to a cutoff energy
$E_{\text{cut}}$ of 450.0 eV. Due to the large size of the supercells used
in our ab initio simulations, the Brillouin zone was sampled
by the $\Gamma$ point only. Besides this, our calculations were di-
pole corrected by using a dipole sheet in the middle of the
vacuum slab.

To investigate the structural stability of the pyridine on
the Cu(110) and Ag(110) surfaces, we focused mainly on two
different perpendicular adsorption configurations determined
by a parallel orientation of the molecular plane to the [001]
(hereafter denoted as [001] adsorption geometry) and [110]
(hereafter denoted as 110 adsorption geometry) crystallo-
graphic directions. Besides these, perpendicular geometries
we also considered several parallel adsorption configurations
such that the molecular plane is parallel to Cu(110) and
Ag(110) surfaces. The relative stability of these adsorption
genometries can be assessed from the calculated adsorption
energy $E_{\text{ads}}$ defined as

$$E_{\text{ads}} = E_{\text{sys}} - E_{\text{pyridine}} - E_{\text{Cu,Ag}[110]},$$

where $E_{\text{sys}}$ represents the total energy of the relaxed
pyridine-(110) metal surface system, $E_{\text{pyridine}}$ is the total energy
of the isolated pyridine molecule, and $E_{\text{Cu,Ag}[110]}$ are the
total energies of the isolated Cu(110) and Ag(110) sur-
faces, respectively.

A final note concerns the role of the long-range van der
Waals interactions on the geometry and adsorption energy of
the pyridine-metal system. In the present study we consid-
ered these effects by employing the semiempirical approach
proposed by Grimme. This method relies on corrections
added to the DFT-GGA total energy and forces derived from
a damped atom-pairwise potential $C_6 R^{-6}$ ($C_6$ represents
the dispersion coefficient for a given atom pair and $R$ is the
distance between the atoms). The self-consistent calculated
van der Waals energy and forces were then used during the
structural relaxations of the pyridine on metal surfaces under
consideration. Notice that the semiempirical method em-
ployed in our study to account for the van der Waals inter-
actions is similar to that developed by Ortmann et al. and
used, for instance, to investigate the adsorption of adenine
on graphite(0001) surface.

III. RESULTS AND DISCUSSION

A. Pyridine in gas phase

As a preliminary step of our study, we optimized the geo-
metry of the pyridine molecule in the gas phase using an
orthorhombic supercell with dimensions of $20 \times 20 \times 20$ Å$^3$.
The calculated bond lengths and bond angles are presented in
Table I and are in a very good agreement with the experi-
mental data published in Ref. 35. For comparison, in this
table we also list the similar theoretical values obtained by
means of ab initio Hartree-Fock (HF) (Refs. 36 and 37) and
DFT (Ref. 17) methods. While the DFT and HF bond lengths
are almost the same, it seems that the HF method slightly
overestimates the bond angles, most notably for the bond
angle determined by the N, C1, and C5 atoms ($\approx 2\cdot^\circ$).

Since the basic goal of our study is to investigate how the
electronic structures of the pyridine and metal surface change
due to their interaction, in Fig. 5(a) we present the angular-
momentum resolved local density of states (LDOS) calculated
for the C$_5$H$_5$N molecule in the gas phase. Of particular
interest are the frontier orbitals, namely, the highest occupied
molecular orbitals (HOMOs: $\pi_2$, $\pi_1$, and $\sigma$) and lowest un-
occupied molecular orbitals (LUMOs: \( \pi^*_2 \) and \( \pi^*_3 \)). The Cartesian coordinate system was chosen such that the \( \sigma \) and \( \pi \) atomic orbitals are in the molecular plane while the \( \pi \) orbital is oriented perpendicular to it.

With this specification the HOMO is a \( \sigma \)-in-plane molecular orbital, because it consists of a combination of \( s, p_x \), and \( p_y \) atomic orbitals, while the LUMO \( (\pi^*_2) \) is a \( \pi \) molecular orbital since it originates from a \( p_z \) orbital perpendicular to the molecular plane. Note that the bonding orbitals HOMO−1\((\pi_1)\), HOMO−2\((\pi_2)\), and the antibonding one LUMO+1\((\pi^*_3)\) also have a \( \pi \) character. Since the spatial distribution of the charge density corresponding to these molecular orbitals and their nodal structure are key factors in describing the interaction of pyridine with surfaces, in Fig. 1 we present the charge-density plots of \( \pi_2, \pi_1, \sigma, \pi^*_2, \) and \( \pi^*_3 \) orbitals [see also Fig. 5(a)]. Note the accumulation of charge density around the N atom in the case of HOMO and the presence of a nodal plane in the molecular plane in the case of HOMO−2, HOMO−1, LUMO, and LUMO+1. The relevance of these features on the mechanism of the pyridine adsorption on the studied metallic surfaces will be emphasized later.

### B. Ground-state geometry and energetics

As mentioned in Sec. I, the pyridine molecule can adsorb on surfaces with its molecular plane perpendicular or parallel to the substrate under consideration. In the former case the adsorption process involves the nitrogen lone-pair electrons (\( \sigma \)-like molecular orbital), while in the latter case it is due to the \( \pi \)-like molecular orbital. Another possibility is represented by a tilted adsorption geometry which implies the presence of both lone-pair and \( \pi \)-like interactions with the surface. On the Ag(110) surface, the isolated C\(_5\)H\(_5\)N molecule adsorbs via its nitrogen lone-pair orbital.\(^{22}\) Similarly, in the case of the Cu(110) surface, some experimental studies\(^{23,24}\) suggest also a perpendicular adsorption geometry even if a tilted configuration cannot be ruled out.\(^{19}\) Therefore, in this section we analyze the strength of the pyridine-substrate interaction when the molecular plane is oriented perpendicular or parallel to the surface.

The calculated adsorption energies \( E_{ads} \) of a single pyridine molecule on the Cu(110) and Ag(110) surfaces are reported in Table II. The analysis of these values clearly shows that for both surfaces, the perpendicular adsorption configuration corresponding to the molecular plane aligned parallel to the [001] direction is the ground-state geometry (see Fig. 2). A larger adsorption energy calculated for the C\(_5\)H\(_5\)N on the Cu(110) surface than that obtained when it is adsorbed on the Ag(110) one suggests a stronger molecule-substrate interaction in the former case. This behavior can be traced back to a different strength of the hybridization between the HOMOs

<table>
<thead>
<tr>
<th>Surface</th>
<th>Orientation</th>
<th>Adsorption energy ( E_{ads}^{PBE} ) (eV)</th>
<th>Adsorption energy ( E_{ads}^{PBE+vdW} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(110)</td>
<td>[001]</td>
<td>−0.758</td>
<td>−0.972</td>
</tr>
<tr>
<td></td>
<td>[110]</td>
<td>−0.629</td>
<td>−0.842</td>
</tr>
<tr>
<td></td>
<td>flat</td>
<td>−0.381</td>
<td>−0.673</td>
</tr>
<tr>
<td>Ag(110)</td>
<td>[001]</td>
<td>−0.447</td>
<td>−0.595</td>
</tr>
<tr>
<td></td>
<td>flat</td>
<td>−0.758</td>
<td>−0.972</td>
</tr>
</tbody>
</table>
LUMO + 1 (π2*)  LUMO (π1*)

HOMO (σ)

HOMO − 2 (π2)  HOMO − 1 (π1)

HOMO − 3 (σ)

FIG. 1. (Color online) Contour plots of several molecular orbitals of the pyridine molecule in the gas phase. The HOMO and HOMO − 3 are σ-type molecular orbitals being combinations of s, pz, and px atomic type orbitals. The HOMO−2(π2), HOMO − 1(π1), LUMO (π1*), and LUMO+1(π2*) are π-type molecular orbitals having a node in the plane of the molecule, because they originate from a px atomic type orbital. Note that px and py atomic orbitals are in the molecular plane while the pz is oriented perpendicular to it [see also text and Fig. 5(a)].

and the d band of the substrate (see Sec. III D).

A stronger molecule-substrate interaction for pyridine on the Cu(110) surface than on the Ag(110) one is also apparent from the analysis of the geometry of the adsorbed molecule on these surfaces. The average metal-molecule surface distances are shorter in the case of the Cu(110) as compared to the Ag(110) substrate (≈0.33 Å for the perpendicular and ≈0.5 Å for the flat adsorption geometries, respectively). As presented in Table I, one can also observe that, as compared to the molecule in the gas phase, for the pyridine adsorbed on the Cu(110) surface the molecular structure is more distorted than that obtained in the case of C5H5N on the Ag(110) surface.

Besides these general observations, the bond lengths and bond angles are practically independent on the orientation of pyridine molecular plane (along the [001] or [110] directions). This feature corresponds to a small adsorption energy difference between these configurations for each studied (110) surface.

Although an [001] adsorption geometry is energetically more favorable than the [110] adsorption one, the energy difference between these two different conformations is rather small. In particular, for the Ag(110) surface this energetic difference (≈0.066 eV) is comparable to the thermal energy at room temperature (kBT=0.026 eV), which raises the question if the pyridine molecule can fluctuate between these configurations.

To shed light on this problem we analyzed the energy barrier corresponding to a stepwise rotation of the molecular plane from the [001] adsorption geometry to the [110] one (see Fig. 3). At each step the pyridine-substrate geometries were relaxed in a direction perpendicular to the surface. One can observe a marked different behavior depending on the chemical nature of the metallic surface under consideration. For C5H5N on Ag(110) surface there is a smooth transition when rotating the molecular ring from the [001] adsorption geometry to the [110] one. On the contrary, a similar rotation for pyridine on the Cu(110) surface reveals that the [110]
The adsorption configuration is a local minimum separated by an energy barrier of \( \approx 0.55 \) eV from the [001] adsorption geometry.

It is interesting to note that, starting with an initially flat geometry of pyridine on the Cu(110) and Ag(110) substrates, the geometry of the final relaxed configuration sensitively depends on the position of the N atom on the surface. As presented in Figs. 4(a)–4(c), when the N atom is placed close to a surface atom or above it, the molecule-substrate interactions lead to a relaxed geometry with the heterocyclic ring perpendicular to the surface [see Fig. 4(d)]. In comparison to the ground-state geometry, this adsorption configuration has the molecular plane twisted with an angle of \( \approx 21.7^\circ \) with respect to the [001] direction. Such an adsorption geometry is similar to that obtained for the Cu(100) surface,\(^\text{18}\) however, in the latter case it represents the ground-state configuration. The lift of the molecular plane from a parallel to a perpendicular adsorption geometry evidenced in our \textit{ab initio} study is a clear fingerprint of a competition between the \( \sigma \)- and \( \pi \)-like interactions of the pyridine molecule with the Cu(110) and Ag(110) surfaces.

However, when the N atom lies between the surface atoms [see Figs. 4(e)–4(g)], the pyridine molecule relaxes to a geometry with the molecular plane almost parallel to the Cu(110) and Ag(110) surfaces. In the most stable flat configuration depicted in Fig. 4(g), the average vertical distance between the molecule and the surfaces is \( \approx 3.0 \) Å in the case of the Cu(110) substrate and \( \approx 3.2 \) Å for the Ag(110) one. An additional difference consists in a slightly larger angle between the molecular plane and the Ag(110) surface (\( \approx 9^\circ \)) than that on the Cu(110) one (\( \approx 3^\circ \)).
N close to a copper atom of a [110] row

FIG. 4. (Color online) Several flat adsorption configurations of the pyridine molecule on Cu(110) and Ag(110) surfaces. The (a), (b), and (c) starting configurations with the N atom of the molecule close to a copper atom of a [110] row relax to a local minimum geometry such that the pyridine is perpendicular to the metal surface as shown in (d). In the (e), (f), and (g) starting geometries the relaxed pyridine molecule remains flat on the surface. In this case the most stable local minimum corresponds to configuration (g) where the N atom is above two adjacent [001] rows.

side views of the flat ground state geometry (g)

along [110] along [001]

PBE(DFT)+vdW

i.e., (a) are the orbitals slightly broadened and still keep their localized molecular character or (b) broad bands with mixed metallic and molecular character are formed.

In order to investigate the bonding mechanism of the pyridine on Cu(110) and Ag(110) surfaces we first identified the LDOS for the adsorbed molecule-substrate system by summing over all atomic contributions. The corresponding calculated LDOS for the perpendicular and flat adsorption are reported in Figs. 5(b) and 5(c), respectively. The energy range of interest for understanding the coupling of the C5H5N molecule to the Cu/Ag(110) surfaces through metal d bands is from −5.5 to −1.0 eV below Fermi level. Since in the case of the perpendicular adsorption geometry the structural changes induced by van der Waals corrections are neg-
ligible, in the following we will focus on the electronic structure obtained without these corrections. On the contrary, as such corrections are very important for the flat adsorption geometry its electronic structure is analyzed while taking into account these dispersion effects.

The analysis of LDOS for the perpendicular adsorption configuration reveals that in the case of both substrates, the bonding mechanism involves a strong hybridization of pyridine HOMO ($\sigma r$ orbital) and HOMO−2 ($\pi_2$ orbital) (see Fig. 1) with the $d_{z^2}$- and $d_{x^2}$-type orbitals of the substrate, respectively. The interaction of HOMO−1 ($\pi_1$) with the $d_{z^2}$-type orbital is weaker and in consequence, this molecular orbital is not pushed as low in energy as compared to the HOMO ($\sigma r$) and HOMO−2 ($\pi_2$). We would like to emphasize that HOMO−1 ($\pi_1$) does not interact as strongly as HOMO−2 ($\pi_2$) because it has no electron distribution on N atom. Therefore it is expected that its contribution to the N-metal binding is negligible, while HOMO−2 ($\pi_2$) has a considerable amount of electron density on the N atom and interacts more effectively with the metal orbitals.

On the contrary, for the flat adsorption configuration, the LDOS analysis shows that the strong hybridization of HOMO−1 ($\pi_1$) and HOMO−2 ($\pi_2$) with the metal $d$ states results in broad bands with mixed metallic and $\pi$ molecular characters. The interaction of the pyridine HOMO ($\sigma r$) with the metal is much weaker, and in consequence this orbital remains localized mainly on the molecule.

As a general characteristic for both perpendicular and flat adsorption configurations, the lowest unoccupied molecular orbitals $\pi_1^*$ and $\pi_2^*$ or the antibonding band $\pi_{1,2}^*$ [see Figs. 5(b) and 5(c), respectively] do not play a role in the bonding process since they remain unoccupied in the moleculesubstrate system. This is a clear proof that the pyridine-surface interaction has a strong covalent character. Indeed, if the LUMOs were partially or fully occupied then a strong ionic interaction between metal and molecule would take place.

However, there is a significant difference between the electronic structure of the pyridine on the Cu(110) surface with respect to that on the Ag(110) one. As already mentioned, for the perpendicular adsorption the N–Cu bond length is much smaller than that of the N–Ag one. This structural detail is the first evidence that the C$_6$H$_5$N-Cu(110) surface interaction is much stronger than the C$_6$H$_5$N-Ag(110) one. A stronger molecule-substrate interaction for the C$_6$H$_5$N-Cu(110) system is also obvious from the analysis of its electronic structure. As presented in Fig. 5, the main bonding orbital ($\sigma_1$) is pushed to much lower energies for the Cu surface (−4.7 eV) as compared to the Ag one (−2.5 eV). This effect can be understood starting from the observation that the $d$ bands of the Cu(110) surface lie closer to Fermi level than those of the Ag(110) substrate. In a Schottky–Mott barrier model, this implies that the pyridine HOMO is closer in energy to the $d$ bands of the Cu(110) substrate than those of the Ag(110) surface. In consequence, this molecular orbital interacts more strongly with the Cu(110) surface than with the Ag(110) one, leading to a larger energy splitting in the former case and thus to a larger adsorption energy for the C$_6$H$_5$N on the Cu(110) surface than on the Ag(110) one.

An intuitive chemical view of the nitrogen-metal-atom interaction is presented in Fig. 6. It shows that the interaction of the $d_{z^2}$ orbital of the metal and the HOMO ($\sigma r$) orbital of the pyridine is independent of the molecular plane orientation. Moreover, the hybridizations along the [001] or [110] directions between the $d_{z^2}$ or $d_{x^2}$ orbital of the metal surface and the HOMO−2 ($\pi_2$) orbital are equivalent. So, within this simple model, it is expected that the total energies of the [001] and [110] configurations are equal. In reality, this degeneracy is slightly shifted in the presence of the substrate due to a different surface environment when the molecular plane lies along the [001] or [110] directions. Nevertheless, the rather small energy difference between these two perpendicular configurations indicates a strong local character of the interaction between the nitrogen and the surface metal atom.

As a characteristic of the copper surface, when rotating the molecular plane from [001] toward the [110] direction, the overlap between $d_{yz}$ and HOMO−2 ($\pi_2$) will decrease and therefore the total energy of the system will increase (see Figs. 3 and 6). By further rotating the molecular plane toward [110] the bonding overlap between $d_{yz}$ and $\pi_2$ starts to increase and therefore the total energy of the systems will decrease. Thus, the high energy barrier between the [001] and [110] configurations shown in Fig. 3 indicates a strong $d_{yz} - \pi_2$ interaction for the Cu(110) surface. On the contrary, the low energetic barrier in the case of Ag(110) surface shows that the $d_{yz} - \pi_2$ interaction is quite weak and there-
fore the bonding takes place mostly through $d_{z^2}$ orbital of the metal and the HOMO ($\sigma_1$) orbital of the pyridine. Therefore, we can assume that, when the perpendicular adsorbed molecules are arranged in a closely packed self-assembled monolayer, the van der Waals intermolecular interactions will play the major role for the Ag(110) as compared to the Cu(110) surface.

For the flat adsorption geometry, due to the van der Waals interactions, the average molecule-surface distance is much smaller ($\sim$0.5 Å) for the Cu(110) as compared to the Ag(110) surface. As in the case of perpendicular adsorption geometry, this indicates a stronger interaction between the molecule and the copper surface. This effect is also easily seen in the LDOS characteristics in Fig. 5(c), which shows that the $\pi_{1,2}$ bands are shifted lower in energy for the copper surface as compared to the silver one.

The basic features displayed by the LDOS of the C$_5$H$_5$N molecule on Cu/Ag(110) surfaces may be easily understood in terms of the Anderson-Newns model, which describes the interaction of a localized molecular orbital with the metal states. In the case of a metal with a completely occupied $d$ band (Cu and Ag), this model predicts that both bonding and antibonding molecular orbitals are formed, analog to the bonding and antibonding molecular orbitals formed by two interacting atoms. As shown already for other molecules, which use the carboxylate group to anchor to the Cu(110) surfaces, [15,16] also in the case of the pyridine molecule adsorbed on the Cu(110) surface an effective hybridization between molecule’s HOMO with the $d$ bands of the metal occurs and the bonding process can be seen as a chemisorption one. A schematic view of the pyridine interaction with Cu(110) or Ag(110) metal surfaces for the perpendicular and flat adsorption geometries in terms of this model is presented in Fig. 7(a) and 7(b), respectively.

IV. SUMMARY

In the present study we focused on an ab initio investigation of the adsorption mechanism of the pyridine (C$_5$H$_5$N) on the Cu(110) and Ag(110) surfaces. The pyridine molecule can bind to these substrates via its nitrogen lone-pair electrons or through its planar $\pi$-like molecular orbital leading to a perpendicular or parallel adsorption geometry, respectively. Our first-principles calculations clearly show that, in the ground state, the heterocyclic ring of C$_5$H$_5$N is perpendicular to the Cu(110) and Ag(110) surfaces and it is aligned along the [001] surface direction. However, when starting with a parallel adsorption configuration, the geometry of the relaxed molecule-surface system depends significantly on the position of the N atom on the Cu(110) and Ag(110) surfaces. More specifically, when the N atom is placed close to a surface atom or above it, in the final relaxed geometry the heterocyclic ring of pyridine molecule is perpendicular to both surfaces. However, when the N atom is between the surface atoms, the molecule remains flat on these substrates. Since in the latter case the molecule-surface interactions take place through the planar aromatic $\pi$-like molecular orbital, we analyzed the role of the van der Waals interactions on the bonding process of pyridine on Cu(110) and Ag(110) surfaces by employing a semiempirical method. We prove that the dispersion effects corresponding to the long-range van der Waals interactions play an important role from both geometrical and energetic point of views. In the case of the perpendicular adsorption configurations, the inclusion of van der Waals forces leads essentially to the same relaxed geometries, while a van der Waals-corrected energy functional (PBE+vdW) lowers the adsorption energy by $\sim$0.2 eV on

FIG. 7. (Color online) Schematic view of the hybridization of pyridine molecular orbitals with Cu(110) and Ag(110) $d$ bands. (a) In the case of the perpendicular adsorption geometry, the pyridine molecule binds to surface mainly via the $\sigma_1$ molecular orbital. For the Cu(110) surface this orbital is drastically shifted to lower energies, well below the $\pi_1$ and $\pi_2$ orbitals, while for the Ag(110) surface the $\sigma_1$ orbital gives rise to a peak with small weight above the $\pi_1$ and $\pi_2$ orbitals and a broad $\sigma$-type bond having also a small intensity [see also Fig. 5(b)]. (b) In the flat adsorption geometry the strong hybridization of the $\pi_1$ and $\pi_2$ molecular orbitals with the metal $d$ bands leads to the formation of broad bonding $\pi_{2,1}$ and antibonding $\pi_{1,2}$ bands with mixed $\pi$ and metallic character. However, the shift toward lower energies of the occupied $\pi_{2,1}$ band is larger for the copper than for the silver surface. This effect is due to a much stronger hybridization of the $\pi$ molecular orbitals with the $d$ bands of the metal surface in the former case [see also Fig. 5(c)].
ROLE OF THE VAN DER WAALS INTERACTIONS ON THE
both surfaces. On the contrary, in the case of the parallel adsorption geometries, the van der Waals corrections have a substantial impact on the geometry of the relaxed configurations and on the corresponding adsorption energies. From the electronic structure point of view, for the ground-state perturbations and on the corresponding adsorption energies. From the substantial impact on the geometry of the relaxed configuration, where the interaction of the HOMO


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