PHYSICAL REVIEW LETTERS

Coulombic Amino Group-Metal Bonding: Adsorption of Adenine on Cu(110)

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(Received 22 December 2004; published 16 June 2005)

The interaction between molecular amino groups and metal surfaces is analyzed from *first-principles* calculations using the adsorption of adenine on Cu(110) as a model case. The amino group nitrogens are found to adsorb on top of the surface copper atoms. However, the bonding clearly cannot be explained in terms of covalent interactions. Instead, we find it to be largely determined by mutual polarization and Coulomb interaction between substrate and adsorbate.

Knowledge of the interaction between biologically active molecules, such as proteins or nucleic acid, and solid surfaces is relevant to the preparation of biocompatible materials and biosensors. The adsorption of small organic molecules, in particular, amino acids or nucleic acid bases, on metal surfaces [1–6] is thereby studied to help in the understanding of complex intermolecular processes, e.g., in the origin of life research [7].

While the geometrical structure of molecular overlayers can be reliably identified, still no coherent picture of the underlying bonding processes has evolved, despite a large amount of data. Organic molecules adsorb qualitatively differently on metals than on semiconductors, where covalent bonds prevail. In fact, the question of how organic molecules bond to metal substrates has recently become a topic of intense research and controversial discussion [8–17]. A recent review has been given by Nilsson and Pettersson [18].

The bonding of molecular amino groups to metal surfaces is thereby of particular interest and has given rise to a number of interpretations. In solution its formation may depend on the pH value [19]. Also, the influence of electric fields on the bonding was observed [20]. These experimental findings are in accord with the relatively low energy gain upon bonding between molecular amino groups and metal substrates: 0.26 eV were calculated for cysteine adsorbed on Au(111) [21] and, depending on the enantiomer and bonding configuration, 0.1–0.4 eV were predicted for 2-amino-3-dimethylphosphino-1-propanethiol on Au(17 11 9) [22]. The bonding between the cysteine amino group and Au(111) has been interpreted in terms of the Anderson-Newns model, which describes the interaction of a localized atomic orbital with extended metallic states [21]. Because of the molecule-metal hybridization, the adsorption process may thus be understood as chemisorption with strong covalent contributions. This is somewhat in contrast, however, to the relatively low energy gain upon amino group-metal bonding. For ammonia on Cu(110) the adsorption energy seems to be somewhat higher. Here a bonding energy of 0.78 eV was calculated and explained by both covalent and ionic contributions [8].

A similar energy is reported for the bond formed between the amino group of glycine and the Cu(110) surface [23]. It has been explained by the formation (and partial occupation) of bonding and antibonding combinations of the N $2p_z$ orbital with the metal valence d band.

The question of what governs the bonding between molecular amino groups and metal surfaces is addressed in this Letter. The adsorption of adenine on Cu(110) has been chosen as the model system, because it is well characterized by scanning tunneling microscopy, low-energy electron diffraction, electron energy loss spectroscopy, as well as cluster calculations, and it serves as a case study for enantiomeric interactions on solid surfaces [2,3]. On the basis of accurate total-energy and electronic-structure calculations, we argue that the bonding is not covalent, but can nevertheless be explained within a simple and intuitive picture: The charge transfer from the molecule to the substrate as well as the mutual polarization of the amino group N lone pair of electrons and the metal substrate lead to a preferred-site interaction that largely accounts for the bonding energy calculated from *first principles*.

The calculations are performed using density-functional theory within the generalized gradient approximation (DFT-GGA) [24] as implemented in the Vienna *Ab Initio* Simulation Package (VASP) [25]. The electron-ion interaction is described by the projector-augmented wave [26] scheme. It allows for the accurate treatment of first-row elements as well Cu $3d$ electrons with a relatively small energy cutoff. The electronic wave functions are expanded into plane waves up to a kinetic energy of 25 Ry. The Cu(110) surface is modeled with periodically repeated slabs. Each supercell consists of six atomic layers of copper plus adsorbed adenine molecule and a vacuum region equivalent in thickness to 44 atomic layers. All calculations are performed at the theoretical lattice constant of 3.6368 Å using a $p(3 \times 4)$ surface periodicity to minimize the molecule-molecule interaction between neighboring supercells. The uppermost two copper layers as well as the molecular degrees of freedom are allowed to relax. The Brillouin zone integrations are restricted to the Γ point.

The full geometry optimization starting with the adenine molecule [see Fig. 1(a)] lying flat above the Cu(110) surface with a vertical distance of 2.0 Å results in the structure schematically shown in Fig. 1(b). The potential energy surface sketched in Fig. 1(d) shows significant structures. For adenine the copper rows are separated by an energy barrier of about 0.5 eV, and the most favorable bonding position is reached when the amino group nitrogen is directly above a copper atom. The N-Cu bonding direction has an off-axis angle of 2.9° with respect to the surface normal.

From Fig. 1(b) it can also be seen that the adsorbed adenine molecule in equilibrium position is noticeably deformed with respect to its nearly planar gas-phase structure [27,28]. Upon bonding to Cu(110) the molecule assumes a strongly tilted geometry with the amino group NH$_2$ bent by 17.7° and the rest of the molecule [29] by 26.4° with respect to the surface plane. In contrast to gas-phase adenine, the amino group nitrogen is nearly tetrahedrally coordinated with angles ranging from 112.6° to 113.4°; see also Fig. 1(c). This is typical for sp^3 hybridized atoms. Indeed, the wave-function analysis for nitrogen indicates nearly sp^3 hybridization ($\chi_s = 0.31$, $\chi_{p_x} = 0.23$, $\chi_{p_y} = 0.22$, and $\chi_{p_z} = 0.24$). The computational results

concerning the molecule tilting agree with the interpretation of vibrational spectroscopy experiments [2]. There are also small structural changes in the substrate: The Cu atom that bonds to the amino group moves out of the surface plane by 0.15 Å.

The Cu-N distance of 2.32 Å is consistent with the bond lengths in organometallic Cu-N complexes [30] and slightly larger than the length of 2.10–2.13 Å reported for the respective bond of glycine adsorbed on Cu(110) [23,31]. It certainly exceeds, however, the sum of the covalent radii of Cu and N of about 1.8 Å. Therefore, the bond is unlikely to be covalent. This is corroborated by the wave-function analysis (not shown here), which shows no interface orbitals with clear-cut bonding or antibonding character. Consistent with the large Cu-N distance, we calculate a relatively small adsorption energy $E_{ad} \equiv E_{ads/subs} - E_{ads} - E_{subs} = 0.34$ eV from the energies of the isolated (E_{ads}, E_{subs}) and the total system ($E_{ads/subs}$), indicating at first glance physisorption rather than chemisorption. There are presently no experimental data available on the adsorption energy. However, due to the failure of DFT-GGA calculations to account for van der Waals interaction [32], the actual adsorption energy may be somewhat higher than the calculated 0.34 eV.

In order to elucidate the bonding behavior, we analyze the electron transfer by calculating the spatially resolved charge-density difference,

$$\Delta\varrho(\mathbf{r}) = \varrho_{ads/subs}(\mathbf{r}) - \varrho_{subs}(\mathbf{r}) - \varrho_{ads}(\mathbf{r}), \qquad (1)$$

where $\varrho_{ads/subs}$, ϱ_{subs}, and ϱ_{ads} are the (negative) charge densities of the relaxed adsorbate-substrate system, of the clean relaxed surface, and of the adsorbate without substrate, respectively. From the quantity (1) the number of transferred electrons,
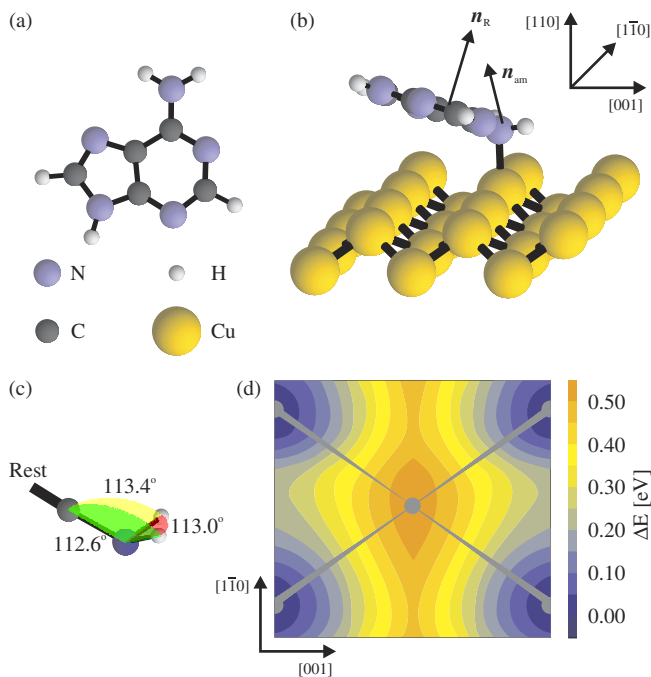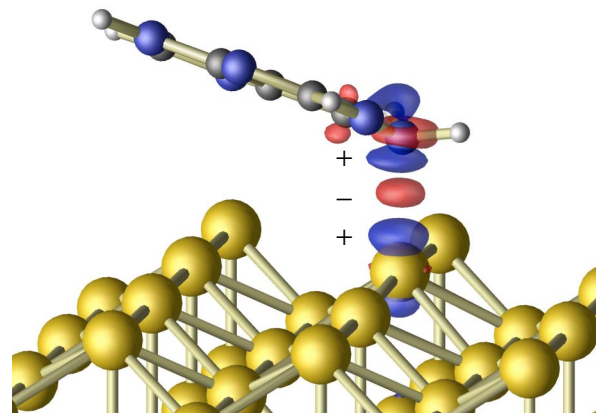

FIG. 1 (color online). (a) Sketch of the adenine molecule and (b) the optimized adsorption geometry of adenine on Cu(110). Blue (dark gray, light gray, golden) spheres correspond to N (C, H, Cu) atoms. (c) Angles of amino group pyramidalization of adsorbed adenine. (d) The potential energy surface [legend gives energy above the minimum; blue (0.00 eV)/red (0.50 eV) indicate favorable/unfavorable adsorption sites] seen by the adsorbed adenine molecule. The positions of the uppermost Cu atoms of one surface unit cell are indicated.

FIG. 2 (color online). Total charge-density difference plot. Regions of electron accumulation/depletion are displayed in blue (+)/red (−) isosurface value: ±0.02 $e/$Å^3. Note the slight elevation of the Cu atom to which the bond is established.

$$Q^{\pm} = \int_{\Delta\varrho(r)\gtrless 0} dr\Delta\varrho(r), \qquad (2)$$

the components of the length of the dipole spanned by Q^+ and Q^-,

$$d_i = \frac{1}{Q^+}\int_{\Delta\varrho(r)>0} dr x_i \cdot \Delta\varrho(r) - \frac{1}{Q^-}\int_{\Delta\varrho(r)<0} dr x_i \cdot \Delta\varrho(r), \qquad (3)$$

and the dipole moment components $p_i = |Q^{\pm}|d_i$ are derived. The adsorption-induced charge-density difference (with respect to the isolated but adsorptionlike deformed molecule) is shown in Fig. 2. There is a net electron transfer from the molecule to the surface of $|Q^{\pm}| = 0.49e$, where Q^+ and Q^- are separated by $\boldsymbol{d} = (-0.87, 0.02, 0.73)$ Å, resulting in an overall dipole moment of $\boldsymbol{p} = (-2.02, 0.05, 1.73)$ D; $|\boldsymbol{p}| = 2.66$ D. (Vector components are parallel to [001], [1$\bar{1}$0], and [110], respectively; see Fig. 1.)

The charge redistribution is related to the molecular structure. The atoms forming the 5- and 6-membered rings of adenine form a partially delocalized highest occupied molecular orbital π-electron system confined to the molecule. The amino group is not part of a ring structure and contains a p_z-like lone-pair orbital which acts as the center of reactivity. In particular, the rehybridization of the nitrogen atom from sp^2 to sp^3 allows for the easy transformation of charge to the down side of the molecule, facing the Cu surface. This in turn polarizes the substrate. We will show in the following that this mutual polarization gives rise to electrostatic interactions that are largely responsible for the bonding between adenine and the metal surface.

It is obvious from Fig. 2 that the charge redistribution cannot simply be explained in terms of ionic bonding. We therefore rationalize it by separately studying the substrate and molecule-related charge-density changes in two virtual subsystems, denoted as I and II, as indicated in Fig. 3. The dividing plane is placed halfway between Cu and N atoms. This allows for the expansion of the electrostatic interactions between the molecule and the substrate into a series of multipole terms. As an example, we show the substrate dipole induced by the adsorption of adenine in the right panel of Fig. 3. The choice of the dividing plane is not unique. Test calculations showed, however, that the precise location of the plane is of minor importance.

The dipole moments in the two subsystems calculated according to the aforementioned procedure give rise to the interaction energy

$$E_{\mathrm{dipole}} = \frac{(\boldsymbol{p}_{\mathrm{I}}\boldsymbol{p}_{\mathrm{II}})R^2 - 3(\boldsymbol{p}_{\mathrm{I}}\boldsymbol{R})(\boldsymbol{p}_{\mathrm{II}}\boldsymbol{R})}{R^5}, \qquad (4)$$

where $\boldsymbol{R}$ is the distance vector between the two dipoles. Together with the monopole term from the overall charge transfer, this accounts for the major part of the electrostatic interaction responsible for the bonding. In the equilibrium position, one obtains for the total Coulomb energy $E_C = E_{\mathrm{mono}} + E_{\mathrm{dipole}} = -1.47\ \mathrm{eV} + 0.24\ \mathrm{eV} = -1.23\ \mathrm{eV}$; i.e., the electrostatic interaction is dominated by the attractive ionic term, but modified by a mildly repulsive dipolar term.

Since the bonding of adenine on Cu(110) is the result of complex interplay between structural changes and charge transfer within the constituents, we also have to bear in mind the deformation energies. They will reduce the energy gain due to electrostatic interactions. This has been pointed out already for various hydrocarbons adsorbed on metal substrates; see, e.g., Refs. [18,33]. In the equilibrium position it costs about $E_{\mathrm{strain}} = 0.65\ \mathrm{eV}$ strain energy to deform the "ideal" constituents into the final bonding geometry. Together with the electrostatics this results in a total-energy gain upon adsorption of $E_C + E_{\mathrm{strain}} = -0.58\ \mathrm{eV}$. This value is of the same order of magnitude as the (negative) adsorption energy calculated from first principles.

Figure 4 shows the reaction pathway of adsorption, obtained by a series of constrained-dynamics calculations with increasing molecule-substrate distance, together with the aforementioned energy contributions. The reaction coordinate corresponds to the Cu-N distance. If the molecule approaches the surface from infinity, there is a very small energy barrier that can easily be overcome at room temperature. Starting at about 5 Å, the amino group and the metal start to polarize each other, causing an attractive potential to which the molecule is subjected. As seen in Fig. 4, the sum of the attractive Coulomb interaction and the energy required to deform the molecule and the substrate account surprisingly well for the total (negative) adsorption energy until the equilibrium bonding distance is reached.
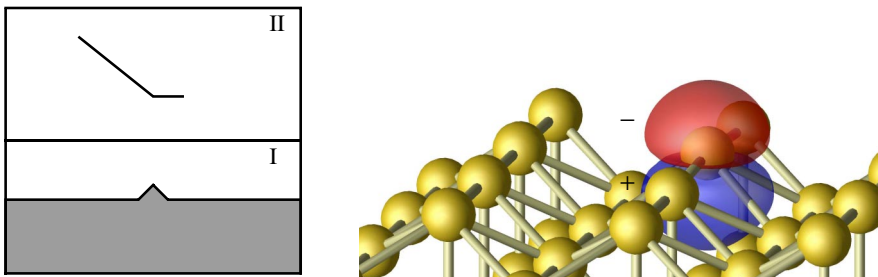

FIG. 3 (color online).   (Left) Decomposition in subsystems I and II (see text). (Right) Charge-density difference with regions of electron accumulation/depletion displayed in blue (+)/red ($-$) isosurface value: $\pm 0.02\ e/\text{Å}^3$, illustrating the dipole accompanying the structural changes in the substrate.
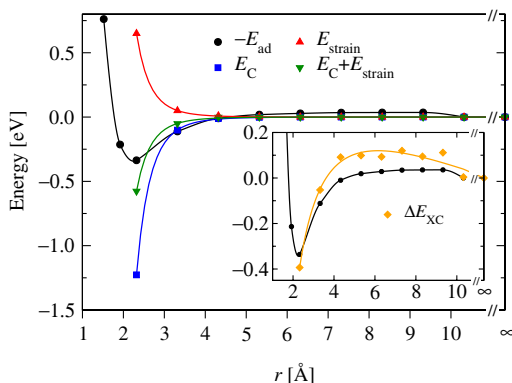
FIG. 4 (color online). Negative adsorption energy (●), strain energy (▲), Coulomb energy (■), and sum of the latter (▼) for adenine adsorbed on Cu(110) as a function of the Cu-N distance. The inset shows the negative adsorption energy compared to the variation of the GGA exchange and correlation energy (◆). Solid lines are guides to the eye.

Obviously, the description of the chemical bonding in terms of such purely classical contributions cannot capture the complete physics of the interactions. This is illustrated in the inset of Fig. 4, where the difference of the GGA exchange and correlation energy relative to the isolated constituents is shown versus the bonding distance. We find a repulsive energy contribution for bonding distances larger than 3.5 Å and an attractive interaction for smaller distances. The magnitude, however, is clearly smaller than that of the Coulomb contribution discussed above. As discussed earlier, the wave-function analysis shows that no major covalent bonding contributions to the total energy can be expected. We thus identify the Coulomb interaction as the main driving force for the bonding between the amino group and the copper surface.

To summarize, we have analyzed in detail the bonding between molecular amino groups and metal surfaces by means of first-principles calculations using the adsorption of adenine on Cu(110) as an example. We calculate an adsorption energy of 0.34 eV, which on one hand is clearly below the values typical for ionic or covalent bonds, but on the other hand exceeds the interaction energies known from van der Waals and even hydrogen bonds. On the basis of the calculated charge transfer characteristics, we explain the bonding as resulting from the combined effects of electrostatic and strain contributions. The peculiar adsorption geometry results from the rehybridization of the amino group nitrogen from sp^2 to sp^3, related to the intramolecular charge transfer.

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