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DFT calculations of adenine adsorption on coin metal (1 1 0) surfaces

E. Rauls *, S. Blankenburg, W.G. Schmidt

Lehrstuhl für Theoretische Physik, Universität Paderborn, 33095 Paderborn, Germany

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ABSTRACT

Density functional theory is used to analyze in detail the adsorption of the adenine molecule on the (1 1 0) surfaces of Cu, Ag, and Au. While the adsorption configurations are similar in all three cases – the molecule bonds via two nitrogen atoms to the substrate – the details like charge transfer or local strain a rather different. The molecule–substrate interaction in case of Cu is stronger than for the more noble metals Ag and Au. Longe-range dispersion forces stabilize the adsorption configuration in dependence on the specific adsorption geometry. In case of Ag and Au, relativistic effects are found to be important.

1. Introduction

The adsorption of organic molecules on metal surfaces is currently intensively investigated, both for reasons of scientific curiosity as well as technological importance [1,2]. Self-organisation of organic molecules appears as one of the most promising approaches to the further miniaturisation of electronic devices. Due to their Watson–Crick complementarity, DNA bases are promising candidates for the design of functional self-organized structures. Two-dimensional structures of self-assembled DNA bases on various substrates, like especially highly oriented graphite or Au(1 1 1) surfaces, have been investigated both experimentally and theoretically to a great extent [3,4]. A large number of studies has been dedicated to single-stranded DNA, immobilized on Au surfaces. Spectroscopic investigations focused on the different adsorption behavior of the different DNA bases on the gold surface [5–8]. The thorough understanding of the molecule–substrate interaction is essential for the understanding and successful prediction of the intermolecular interaction of surface adsorbed molecules [9]. In this context, we investigate here computationally the adsorption mechanism of single adenine molecules on the (1 1 0) surfaces of Cu, Ag and Au.

2. Method

We have performed first principles density functional theory (DFT) calculations using the plane-wave based Vienna ab initio simulation package (VASP) implementation [10]. The electron–ion interaction is described by the projector-augmented wave (PAW) method [11]. The generalized gradient approximation (GGA) [12] is used to model the electron–electron exchange and correlation (XC) part of the energy functional. An energy cut-off of 340 eV has been for the expansion of the wave functions. For the k-point sampling we employed a $(4 \times 4 \times 1)$ Monkhorst–Pack set of k-points. The surface slabs were modelled in (4×3) surface cells with six layers of metal atoms and a vacuum region corresponding to 12 layers. The lowest layer of surface atoms was kept fixed, while all other atoms were allowed to relax freely. In the starting structures, the adenine molecule was placed on the surface in several positions and orientations, which allow the formation of bonds from one or two nitrogen atoms to Cu-atoms of the same (1 1 0) row or of the two adjacent rows. An sp3-like configuration for the amine group was provided, and as angle for the molecule to the surface normal, the position of Ref. [13] was used. The numerical details are thus similar to recent DFT studies on the adsorption of adenine on the Cu(1 1 0) surface [13,14].

In order to understand the chemical trend of the molecular adsorption characteristics with respect to the three substrates copper, silver, and gold, we used two sets of PAW data: both scalar relativistic PAW pseudopotentials as well as PAW data that contain no relativistic effects were used in comparative calculations.

In many instances of organic molecular adsorption on metal surfaces, Coulomb effects have been found to be important [13,15–17]. In order to assess the role of the electrostatic contribution to the molecule–surface bonding, we use an approach similar to the one proposed in Ref. [13]: The adstructure is divided into two regions 1 and 2. The former one contains the admolecule and the other one contains the surface. For these regions, we have

* Corresponding author.
E-mail address: rauls@phys.upb.de (E. Rauls).

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calculated separately the electrical monopoles (q_1 and q_2) and dipoles ($\vec{p_1}$ and $\vec{p_2}$) and evaluated their interactions across the dividing plane

$$E_{\text{mono-mono}} = \frac{1}{4\pi\epsilon_0}\frac{q_1 q_2}{r}, \quad E_{\text{mono-dip}} = \frac{1}{4\pi\epsilon_0}\frac{q(\vec{p}\vec{r})}{r^3},$$
$$E_{\text{dip-dip}} = \frac{1}{4\pi\epsilon_0}\frac{(\vec{p_1}\vec{p_2})r^2 - 3(\vec{p_1}\vec{r})(\vec{p_2}\vec{r})}{r^5} \quad (1)$$

The total electrostatic part of the interaction is then approximated by

$$E_{\text{total}}^{\text{static}} = E_{\text{mono-mono}} + E_{\text{mono-dip}} + E_{\text{dip-dip}} \quad (2)$$

The monopole–dipole term includes both terms for the dipole located in region I or region II, respectively. With this definition, a qualitative understanding of the mechanism can be obtained, while the quantitative values obviously depend on the chosen setup, i.e. the way how the adsorbate system is divided into the two regions. In particular the position of the separating plane has a strong influence on the results. Here, a plane parallel to the metal surface has been chosen that bisects the adsystem at the vertical position of the maximum charge accumulation in the binding region between molecule and surface.

Charge transfer and chemical bonds are, in most cases, well described within DFT with either the local-density approximation (LDA) or the GGA to account for the XC energy of the electrons. This does not hold for dispersion or van der Waals (vdW) forces. Local (LDA) or semilocal XC functionals (GGA) fail to correctly describe the non-classical electronic interactions across regions of very sparse electron densities [18,19]. In particular, it is known from a number of examples (Refs. [20–22]) that dispersion forces, not included in DFT-GGA, have an appreciable impact on molecular adsorption on surfaces. The effect can be expected to be particularly large for cases, where no or relatively few covalent bonds are formed between the adsorbate and the substrate. While it has recently become possible to include such effects in a non-empirical way in DFT calculations for systems of practical interest [22], such calculations are still very expensive from a numerical point of view. On the other hand, simple (semi-)empirical schemes [23–25] based on the London dispersion formula [26], have been shown to yield realistic estimates for the magnitude of the effect that can be expected to result from the inclusion of vdW interaction effects. Because the present study requires the calculation of a large number of different adsorption configurations involving a relatively large molecule of no particular symmetry, such a semi-empirical method is presently the only way to include dispersion interactions. In the present calculations, the implementation described in Ref. [25] has been used to estimate the impact that can be expected to result from vdW forces acting in the specific adsorption geometries. However, a word of caution is in order: Semi-empirical methods to calculate dispersion effects are certainly limited in their accuracy, in particular for metallic systems [27,28].

3. Results and discussion

3.1. Adsorption geometries

Our search for (meta)stable adsorption configurations for adenine adsorbed on the (1 1 0) surfaces of Cu, Ag, and Au resulted in two structures. One of these orientations, called O1 in the following, was already proposed in Ref. [13]. Here the adenine binds with the amine group nitrogen to a metal surface atom, cf. Fig. 1a. However, in addition to O1, a further, even more stable, minimum energy structure exists, called O2 in the following. This orientation features two bonds between molecular nitrogen and metal surface

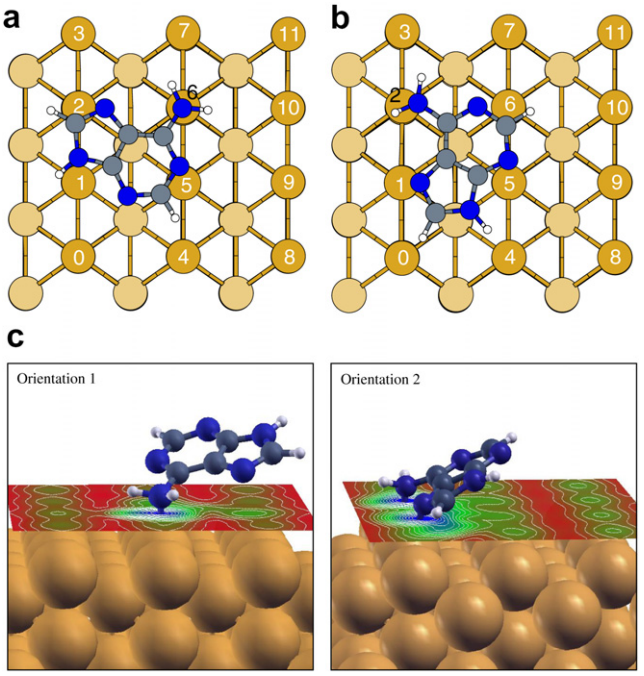

Fig. 1. Schematic top view of the two most stable adsorption orientation O1 (a) and O2 (b) of adenine on Cu, Ag, Au (1 1 0) surfaces are shown in (a) and (b), respectively. One or two bonds form between the molecular nitrogen and surface atom 6 or 1 and 2, respectively. This is also obvious from the valence charge density in the plane between molecule and substrate, shown in (c). Carbon atoms are shown in grey, nitrogen in blue, hydrogen in white. The below lying atoms of the copper surface are shown as dark yellow (top layer) and light yellow (2nd layer), respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

atoms, as shown in Fig. 1b. Here the five and the sixfold ring of the molecule are rotated by approximately 90° compared to O1, and come, thus, to lie closer to parallel to the troughs between the dense packed metal rows. The formation of one or two molecule–substrate bonds is also obvious from the respective charge accumulation shown in the plane between surface and molecule in Fig. 1c a hint on the differently modified electronic properties of the surfaces.

For all three metal surfaces, these two orientations were calculated to be the two most stable adsorption geometries. For both orientations, the angle the molecular plane forms with the substrate varies with the metal. While, for O1, an angle of 26° has been calculated for Cu, the molecule becomes considerably flatter on Ag (13°) and Au (15°), pointing to a less strong rehybridization of the amine-N from the original sp2 to sp3. In O2, the respective angle is 15° in the case of Cu and 7° for Ag and Au.

3.2. Binding energies

Not surprisingly, binding is strongest on the Cu surface. We have calculated the binding energy E_{bind} of a structure as the energy difference between the fully relaxed structure and the fully relaxed isolated fragments. Positive values are defined to be attractive. On Cu, a binding energy of $E_{\text{bind}} = 0.41$ eV has been calculated for O1, which is in good agreement with the value calculated in Ref. [13] (0.34 eV), where only the Γ point had been used for the k-point sampling. The calculated binding energy increases to $E_{\text{bind}} = 0.58$ eV for O2. On the other two metals, the binding energy hardly varies with the orientation: on Ag, the binding energy has been calculated to $E_{\text{bind}} = 0.29$ eV, while, on Au, we have calculated $E_{\text{bind}} = 0.36$ eV (cf. Table 1).

Table 1
Comparison of the binding energies of adenine on Cu, Ag, Au (1 1 0) in orientation O1/O2 with calculations with non-relativistic pseudopotentials for the metals (column 2) and under consideration of additional dispersion correction terms (column 3)

	Relativistic	Non-relativistic	Relativistic + vdW
Cu	0.42/0.58	0.40/0.56	0.43/0.65
Ag	0.26/0.29	0.18/0.17	0.25/0.32
Au	0.31/0.36	0.08/0.25	0.30/0.39

All values in (eV).

3.3. Strain, relativity and dispersion interaction

Heavy elements such as gold – or also silver to some extent – can be expected to be rather susceptible to relativistic effects. In order to see if relativistic effects are important for the organic molecule adsorption, we have repeated the calculations with PAW pseudopotentials that were generated without taking scalar-relativistic corrections into account. As can be seen from the second column in Table 1, we find that indeed the results for Cu do nearly not change. For Ag and Au, however, the situation is very different. The relative stability of O1 and O2 changes in case of Ag, and no bonding at all is observed for adenine in configuration O1 on Au(1 1 0). Altogether, we find the neglect of scalar-relativistic corrections to result in reduced adsorption energies. The strong influence of relativistic effects observed here for organic molecule adsorption on Ag and in particular Au indicates that further corrections might be expected for a fully relativistic description including spin-orbit coupling and kinematic relativistic effects (Darwin and mass velocity terms).

Further corrections to the DFT results can be expected due to the dispersion interaction. In the fourth column of Table 1, the binding energies upon semi-empirical inclusion of vdW effects [25] are compiled for the respective structures. The resulting changes are only small, but in some sense significant: As one would probably expect, the more planar orientation O2 is further stabilized by vdW forces. The energetical difference between O1 and O2 nearly doubles.

Strain contributes substantially to the subtle balance between attractive and repulsive interactions in the present adsorption scenario. We find, however, the relaxation or deformation of the surface and the molecule to be rather different for the three substrate metals. While in case of Cu, structure O1, the adsorbate bonding Cu atom (no. 6 in Fig. 1a) is found to relax out of the surface plane by 0.15 Å (in agreement with Ref. [13]), a slight inwards relaxation of the respective metal atom occurs for Ag (0.06 Å) and Au (0.04 Å). In general, all surface atoms close to the adsorbate show a relaxation in the range of ±0.07 Å. The distance between the metal atom and the amine-N amounts to 2.25 Å for Cu, 2.51 Å for Ag, and 2.45 Å for Au. Also for the O2 structure a strong outwards relaxation of 0.17 Å is observed for atom no. 1 in Fig. 1b in case of Cu. Surface atom no. 2, which binds to the amine-N, relaxes outwards by only 0.05 eV, approximately. For Ag and Au, the latter atom shows again a slight inwards relaxation, while a slight outwards relaxation of atom no. 1 is seen. In both cases, though, the relaxation lies in the range of the relaxation of all surface atoms. The distances between the binding N atoms and the surface atoms are comparable to the O1 case, namely 2.18 (2.13) Å for Cu, 2.57 (2.63) Å for Ag, and 2.53 (2.56) Å for Au for the amine (other) N atom. Comparing the energy that is needed to deform the molecule and the surface from their ideal geometries to their adsorption geometries, we find that for both orientations, the molecular strain is considerably larger than the surface deformation, compare Fig. 2b. In case of Cu, the total deformation energy is 0.10 eV for O1, while 0.23 eV are needed for O2. In case of Ag and Au, the strain energy is smaller and varies less with the orientation: 0.03 (0.06) eV for Ag and 0.04 (0.09) eV for Au in orientation 1 (2). From Fig. 2a, it can be seen that the deformation energy amounts to 24 (40)% of the binding energy on Cu, while the percentage is considerably smaller for Ag and Au with 13 (25)% and 15 (29)%.

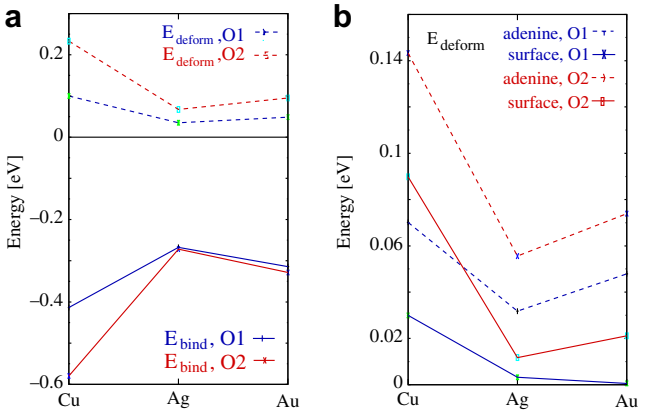

Fig. 2. (a) Comparison of the total deformation and binding energies of adenine on Cu, Ag, Au (1 1 0) surfaces. (b) Deformation energies of molecule and surface for the two orientations.

3.4. Electrostatic effects

In order to understand these differences in the adsorption behavior, we have filtered out the electrostatic interactions between molecule and surface as described in the methods section. All investigations relate to the *induced* charge transfer, obtained by calculating the difference between the charge densities of the fully relaxed structure and the isolated fragments (without further relaxation).

In Fig. 3, the induced charge density is shown for the molecule adsorbed in the two different orientations on the Cu surface. As isovalue, ±0.02 e has been chosen. For Ag and Au (not shown), the picture is similar, but less distinctive.

The calculations show an accumulation of electrons in the binding region between the nitrogen and the metal atom. For the dividing plane located at the maximum of this charge accumulation, we can calculate the net charge transfer (along this line) from the metal surface to the molecule. The largest charge transfer is found for Cu: 0.05 e, while it is only 0.02 e for Ag and Au, in orientation 1. We find 0.05 (0.06) e for the amine (other) N atom in case of Cu, and 0.02 e for each of the N atoms in case of Ag and Au for orientation 2. The total charge transfer from the surface to the molecule in O1

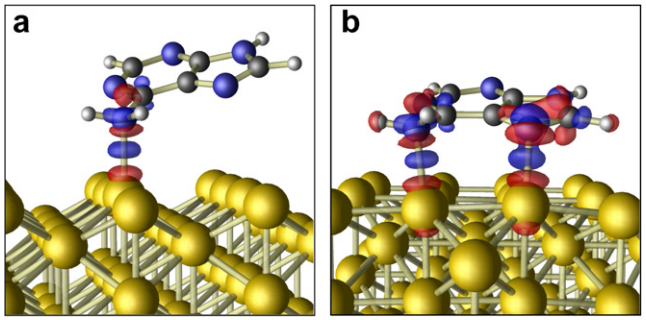

Fig. 3. Induced charge density for adenine on Cu in (a) orientation 1, and in (b) orientation 2, plotted for an isovalue of ±0.02 e, where red denotes (+), blue (−). Strong electron accumulation in the blue regions along the molecule–surface can clearly be seen. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(O2) is 0.12 e (0.20 e) for Cu, 0.12 e (0.16 e) for Ag, and 0.19 e (0.23 e) for Au. Our finding that the *local* charge transfer is clearly largest in case of Cu, does, thus, not reflect itself in the *total* charge transfer. The latter is largest for Au, which only shows a much smaller local charge transfer. This means that the coulombic contribution to the binding energy is clearly larger for the more noble metals, while on the Cu surface, the adsorption is of more covalent character. The analysis of the charge transfer goes along with the corresponding electrostatic contributions to the binding energy. The total electrostatic energy as defined by Eq. (2) is calculated to −0.02 eV for Cu, −0.06 eV for Ag, and −0.12 eV for Au in orientation 1, while it amounts to 0.49 eV for Cu, 0.22 eV for Ag, and 0.55 eV for Au for O2.

The monopole–monopole term and the monopole–dipole terms nearly cancel each other, thus the essential part remains the dipole–dipole interaction. The change of the electrostatic interaction from attractive for O1 to repulsive for O2 can be understood from the respective position of the molecular and substrate dipole: Fig. 4 shows the dipole–dipole interaction for two dipoles of same strength and at constant distance depending on the angles α_1 and α_2 these dipoles have to the surface normal (all redundant constants have been neglected in the plot). In Table 2, the dipoles of surface and molecule, their distances and angles are given for the three metal surfaces and the two orientations, respectively. As can be seen, the angles of the calculated dipoles in the adsorbate structures vary in the shaded area located at the zero-crossing, thus explaining the change in sign between the two orientations.

The molecular and the surface dipole move closer together for O2. Here the strongest reduction of 0.7 Å is found for Cu, while it changes only by 0.4 (Ag) or 0.5 (Au) Å for the other surfaces. Similarly, the strength of both the surface dipole and the molecular dipole changes strongest for Cu. An increase of 0.72 (0.72) eÅ for the surface (molecular) dipole has been calculated for Cu, while the same values are 0.27 (0.41) eÅ for Ag and 0.23 (0.30) eÅ for Au. Thus, already simple electrostatic reflections emphasize the qualitatively different character of the molecule–substrate bond in case of Cu compared to Au or Ag.

For all three metals, the work function

$$\phi = E_{\text{vac}} - E_{\text{Fermi}} \tag{3}$$

where E_{vac} denotes the vacuum level, is found to depend only very slightly on the orientation of the molecule. For the clean surfaces, the calculated work function is 4.47 (4.27, 5.06) eV for the Cu (Ag, Au) (1 1 0) surfaces. These values are in good agreement with experimental values, which themselves show some variation for all three cases. Adenine adsorption reduces the value of the work function to 4.22 (4.20) eV in case of Cu, 4.16 (4.15) eV in case of Ag and 4.94 (4.93) eV in case of Au for O1 (O2). Table 3 summarizes these values. The reduction of the work function upon molecular adsorption seems surprising, given the fact that we determine an electron transfer from the molecule to the substrate in all adsorption scenarios. The resulting dipole layer should increase rather than decrease the work function [29]. However, in the case of molecular adsorption, the molecular dipole itself also modifies the work function, see e.g. Ref. [30]. Comparing the different substrates, we note that the effect of the adsorption induced work function reduction is strongest for Cu (0.25 eV), while it is only about 0.1 eV for Ag and Au.

The total electron density of states (DOS) of the adsorbate structures is nearly independent from the orientation of the molecule but shows clear differences for the three metal surfaces. In Fig. 5 the total DOS is plotted in arbitrary units vs the energy for the

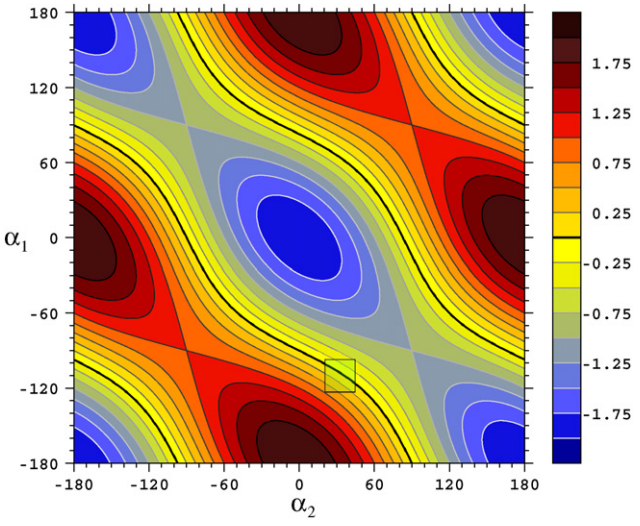

Fig. 4. Angle dependence of the dipole–dipole interaction. Values in (eV).

Table 2
Distances of the calculated dipoles for the three metal surfaces and the two orientations; surface dipole; molecular dipole; angle between the two dipoles

	Cu	Ag	Au
r_{O1} (Å)	4.2	4.1	4.2
r_{O2} (Å)	3.5	3.7	3.7
p_{O1}^{surface} (eÅ)	1.20	1.41	2.13
p_{O2}^{surface} (eÅ)	1.96	1.68	2.36
p_{O1}^{molecule} (eÅ)	1.45	1.55	2.46
p_{O2}^{molecule} (eÅ)	2.17	1.96	2.76
α_1/α_2 (O1)	31.6/117.5	31.3/120.8	34.0/124.9
α_1/α_2 (O2)	29.2/123.6	32.2/127.2	32.5/128.6

Table 3
Calculated values for the work function of the clean metal surfaces and the surfaces with the molecule adsorbed in the two different orientations

Φ	Cu	Ag	Au
Clean	4.47	4.27	5.06
O1	4.22	4.16	4.94
O2	4.20	4.15	4.93

All values in (eV).

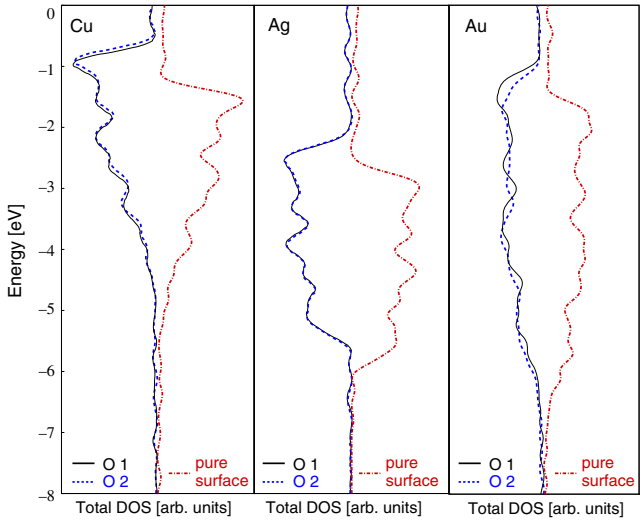

Fig. 5. Total DOS of the adsorbate structures (solid and dashed lines to the left) compared with that of the pure surfaces (dash-dotted lines to the right). The energy has been normalized to the Fermi level of the pure surfaces.

adsorbates in the two orientations for each metal (to the left) and for comparison for the clean surfaces (to the right). For the Cu surface, clearly more states are found at energies close to the Fermi level, while they are much lower for the Ag and the Au surfaces and, especially in the case of Au, also more equally distributed. Upon adsorption, the highest energy peak is shifted by ≈0.65 eV to higher energies in case of Cu and by ≈0.45 eV in case of Ag and Au. Obviously, the total DOS of the Cu surface with its high lying states allows for an energetically easier excitation and renders the Cu surface thereby more reactive than Ag and Au.

4. Summary

To summarize, DFT-GGA calculations predict similar adsorption configurations for adenine adsorbed on the (1 1 0) surfaces of Cu, Ag, and Au. The orientation where the molecule binds via two nitrogen atoms to the substrate is energetically favoured over an orientation where the bonding occurs solely via the amine-group nitrogen. The energy difference between these two configurations can be expected to further increase due to dispersion forces. This is related to the more planar adsorption configuration in orientation 2. In this orientation, the aromatic rings of the molecule are, furthermore, closer to parallel to the (1 1 0) rows of the metal surface. Altogether, the covalent molecule–substrate interaction is stronger for Cu compared to the more noble metals Ag and Au. This holds for the strain, the local charge transfer (along the bond direction), as well as the modification of the electron density of states. The interaction between the N atoms of the molecule and the surface Cu atoms is strong enough to substantially strain both surface and molecule. The finding that the binding energy in spite of this deformation is not only stronger but also more dependent on the orientation in case of Cu compared to Ag and Au, shows that here the binding mechanism is of a more local character in the former case. The electrostatic contribution to the molecule–substrate interaction is appreciable, but complex in nature. It is determined by both the charge transfer from the substrate to the molecule as well as dipole terms which introduce a strong dependence on the molecular orientation. The total charge transfer is larger for Au than for Ag and Cu substrates. The stronger covalent character of the substrate–adsorbate bonding in case of Cu compared to Ag and Au also shows up in the stronger orientation dependence of the total adsorption energy. The Coulomb contribution to the total binding energy is more substantial for Au and Ag and does not lead to a strong structural dependence. Calculations with non-relativistic pseudopotentials for the three coin metals underline the importance of a relativistic description in case of Ag and Au. Essentially no influence was observed in case of Cu.

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References

[1] A. Nilsson, L.G.M. Pettersson, Surf. Sci. Rep. 55 (2004) 49.
[2] W.G. Schmidt, K. Seino, M. Preuss, A. Hermann, F. Ortmann, F. Bechstedt, Appl. Phys. A 85 (2006) 387.
[3] S. Xu, M. Dong, E. Rauls, R. Otero, T.R. Linderoth, F. Besenbacher, Nano Lett. 6 (2006) 1434.
[4] W. Mamdouh, M. Dong, S. Xu, E. Rauls, F. Besenbacher, J. Am. Chem. Soc. 128 (2006) 13305.
[5] T. Yamada, K. Shirasaka, A. Takano, M. Kawai, Surf. Sci. 561 (2004) 233.
[6] H. Kimura-Suda, D.Y. Petrovykh, M.J. Tarlov, L.J. Whitman, J. Am. Chem. Soc. Commun. 125 (2003) 9014.
[7] D.Y. Petrovykh, H. Kimura-Suda, L.J. Whitman, M.J. Tarlov, J. Am. Chem. Soc. 125 (2003) 5219.
[8] D.Y. Petrovykh, V. Perez-Dieste, A. Opdahl, H. Kimura-Suda, J.M. Sullivan, M.J. Tarlov, F.J. Himpsel, L.J. Whitman, J. Am. Chem. Soc. 128 (2005) 2.
[9] S. Blankenburg, W.G. Schmidt, Phys. Rev. Lett. 99 (2007) 196107.
[10] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 6 (1996) 15.
[11] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758.
[12] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671.
[13] M. Preuss, W.G. Schmidt, F. Bechstedt, Phys. Rev. Lett. 94 (2005) 236102.
[14] S. Blankenburg, W.G. Schmidt, Phys. Rev. B 74 (2006) 155419.
[15] H. Öström, L. Triguero, M. Nyberg, H. Ogasawara, L.G.M. Pettersson, A. Nilsson, Phys. Rev. Lett. 91 (2003) 046102.
[16] A. Hauschild, K. Karki, B.C.C. Cowie, M. Rohlfing, F.S. Tautz, M. Sokolowski, Phys. Rev. Lett. 94 (2005) 036106.
[17] A. Alkauskas, A. Baratoff, C. Bruder, Phys. Rev. B 73 (2006) 165408.
[18] H. Rydberg, M. Dion, N. Jacobson, E. Schröder, P. Hyldgaard, S.I. Simak, D.C. Langreth, B.I. Lundqvist, Phys. Rev. Lett. 91 (2003) 126402.
[19] O.A. von Lilienfeld, I. Tavernelli, U. Rothlisberger, D. Sebastiani, Phys. Rev. Lett. 93 (2004) 153004.
[20] Ch. Wöll, K. Weiss, P.S. Bagus, Chem. Phys. Lett. 332 (2000) 553.
[21] F. Ortmann, W.G. Schmidt, F. Bechstedt, Phys. Rev. Lett. 95 (2005) 186101.
[22] S.D. Chakarova-Käck, E. Schröder, B.I. Lundqvist, D.C. Langreth, Phys. Rev. Lett. 96 (2006) 146107.
[23] M. Elstner, P. Hobza, T. Frauenheim, S. Suhai, E. Kaxiras, J. Chem. Phys. 114 (2001) 5149.
[24] M. Hasegawa, K. Nishidate, Phys. Rev. B 70 (2004) 205431.
[25] F. Ortmann, F. Bechstedt, W.G. Schmidt, Phys. Rev. B 73 (2006) 205101.
[26] F. London, Z. Phys. Chem. Abt. B 11 (1930) 222.
[27] J.F. Dobson, J. Wang, B.P. Dinte, K. McLennan, H.M. Le, Int. J. Quant. Chem. 101 (2005) 579.
[28] J.F. Dobson, A. White, A. Rubio, Phys. Rev. Lett. 96 (2006) 073201.
[29] W. Mönch, Semiconductor Surfaces and Interfaces, Springer-Verlag, Berlin, 1995.
[30] K. Seino, W.G. Schmidt, F. Bechstedt, Phys. Rev. B 69 (2004) 245309.