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## A tight-binding model of CO chemisorption on Pd/Ta(110) and similar systems

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**Abstract.** Chemisorption of an isolated CO molecule at various adsorption sites above the epitaxial Pd overlayer on Ta(110), and on related systems, is studied by using a self-consistent tight-binding scheme. Basic assumptions of the model are discussed in detail. The  $\sigma$  donation and especially the  $\pi$  backdonation are generally a good deal reduced at the bimetallic surface as compared with the pure Pd(111) surface. Simultaneously, the bond between CO and the surface becomes weaker. However, for CO in the atop position the effect is considerably smaller than for sites with twofold or threefold coordination and the atop site can therefore become preferred. A simple bonding picture explaining the gross trends is suggested. Core-level shifts induced in surface atoms by the adsorption are briefly discussed.

### 1. Introduction

Chemisorption of CO on the late-transition-metal surfaces is one of the most thoroughly studied surface problems, yet even here unsolved problems remain [1]. Interesting modifications take place when a late transition metal is deposited on a more electropositive transition-metal substrate. Especially rich experimental data for Pd thin films deposited on BCC and HCP substrates are available [2, 3]. In such overlayers the bulk of the Pd d-electron local density of states (LDOS) moves down from the Fermi level  $E_F$  and, simultaneously, a positive core-level shift (CLS) is measured on Pd atoms. Differing explanations have been proposed [2, 3] based either on the charge transfer at the interface or on the hybridization between the overlayer and substrate electronic states, respectively. However, the relationship between the charge transfer and the CLS is not reliable [4] and even the charge-transfer direction can appear to be method dependent. Besides that, effects analogous to those on bimetallic interfaces also exist in alloys due to hybridization. Similar interpretation is consistent with our recent tight-binding calculations [5–7]. Quite recently, elaborate theoretical studies [8–10] have been published that do not find the charge-transfer mechanism to be the decisive one.

The electronic structure changes result in a lower chemical reactivity of the overlayer as documented [2, 3] from H and CO adsorption. The effect correlates well with the LDOS depletion at  $E_F$  and with the sign and magnitude of the CLS. A tentative explanation offers the standard quantum-chemical HOMO–LUMO (the highest occupied versus the lowest unoccupied molecular orbital) reasoning: by moving states away from  $E_F$  one weakens the ability of the system to form new chemical bonds. For the H chemisorption our tight-binding model [11] reproduces the trend correctly.

It is the aim of the present paper to study the CO chemisorption on the Pd surface and overlayers theoretically and to clarify the role of the substrate. We briefly mention the results for Pt as well. To this end self-consistent tight-binding recursion-scheme calculations similar to those in [5–7, 11] are performed. Since the charge transfer is now important, an extension of the previous method is necessary and we refine the model of [12]. Some related results are given elsewhere [13]; the present paper is more detailed and contains additional data that allow us to suggest a clearer interpretation of trends found experimentally and theoretically.

## 2. Model

Previously we have done calculations for Pd and Pt epitaxial overlayers on the (110) face of Ta [6] and W [5] and on the (0001) surface [7] of Re and Ru. Since on Ta(110) the incommensurate hexagonal Pd monolayer is more stable than the epitaxial one [14] we have also considered a mean field model of the incommensurate phase. The approximation ascribed to atoms in the hexagonal Pd overlayer the same averaged interaction with the substrate [11]. We have employed a tight-binding s–d-electron Hamiltonian treated self-consistently within the recursion scheme. The hopping matrix elements were based on an LMTO parametrization and the s electrons were included in order to describe better the overlayer LDOS tail at  $E_F$  originating from the hybridization with the substrate electrons. Only a very small d-electron charge transfer [10, 15] was allowed. A d-electron occupation change at Pd (Pt) adatoms exceeding about  $0.1e$  would spoil the agreement between the calculated LDOS and photoemission spectra. (The d-electron occupation is compared with that in the metallic crystal, not e.g. with the valence configuration  $d^{10}$  of the free Pd atom.) The model was insensitive to assumptions concerning the s electrons on the other hand. We refer the reader to papers [5–7, 11] for details.

We shall study the adsorption of an isolated CO molecule for all systems mentioned and also for the Pd(111) and Pt(111) surfaces. The cases of Pd(111) and Pd/Ta(110) will be considered explicitly.

In Pd(111) the threefold FCC hollow site is the first occupied by CO but at a higher CO coverage the twofold bridge and the single-coordinated atop sites also become populated [16–19]. Pt(111) in the atop position is initially preferred with subsequent adsorption at bridge sites as well [17]; threefold sites appear only under artificial conditions [19, 20]. The molecule is adsorbed upright, with a carbon end. We shall investigate all three adsorption geometries except for that including the hollow site at Pt surfaces. Note that the bridge geometry has not been considered in [13]. We take the experimentally determined metal–carbon distances [16, 17]. Since we have not found complete data for Pd(111) in the literature, we used  $d = 1.85 \text{ \AA}$  for the atop position in analogy to the Pt(111) value [17] and accept the guess [21]  $d = 1.93 \text{ \AA}$  for the bridge site. For CO at Pd (Pt) overlayers the same distances are used.

The method we use has been partly inspired by the Andreoni and Varma model [12]. It relies on the well-known Blyholder picture with chemisorption controlled by the molecular  $5\sigma$  (HOMO) and  $2\pi^*$  (LUMO) orbitals. No other CO orbitals are included.

To construct the CO–metal Hamiltonian hopping elements we consider interactions between the carbon s- and p-electron atomic orbitals and the d orbitals on its first metallic nearest neighbours. The values follow from the universal parametrization proposed by Harrison [22]. Transformation to matrix elements based on the molecular orbitals  $5\sigma$  and  $2\pi^* = \{\pi_x, \pi_y\}$  requires the decomposition of molecular orbitals into atomic ones. We find the necessary information in [23]. The matrix element  $V_\sigma$  describing the molecule–

metal  $\sigma$  interaction for the atop chemisorption on Pd(111) is more than 50% bigger in our calculations than in the model [12] whereas for  $\pi$  interactions there is a good accord. This explains why a very small  $\sigma$  donation to the metal is obtained in the model [12].

Self-consistency is achieved by adjusting the Coulomb integrals (Hamiltonian diagonal matrix elements)  $\epsilon_I = \langle I|H|I \rangle$ . The multi-index  $I = (i, \alpha)$  accounts for both the atomic site  $i$  and the orbital character  $\alpha$ . We suppose the system to have paramagnetic character and omit the spin index. The orbital occupation numbers and LDOS are summed over the two spin orientations—otherwise an additional factor of 2 would appear in some of the formulas below. It is assumed that intra-atomic and intramolecular effects quantified by the adsorbate and metallic Coulomb parameters  $U_a, U_m$  [12, 24] dominate the Coulomb interactions. The Coulomb parameters in metals are much smaller than those in atoms or molecules because of screening; we take the values  $U_a = 6$  eV,  $U_m = 3$  eV from [12]. Similarly, as in [12], we check that the results are not too sensitive to this choice. For the metal d electrons we apply the local-potential (local-density) picture [25] that admits the self-interaction of d electrons:

$$\epsilon_{i\alpha} = \epsilon_{i\alpha}^0 + U_m \Delta N_{id}. \quad (1)$$

In equation (1)  $\epsilon^0$  is the Coulomb integral in the crystal without the adsorbate and  $\Delta N_{id}$  is the d-electron occupation change at site  $i$  due to the adsorption. We calculate the corrections at the nearest and second-nearest metallic neighbours of CO, respectively. As with the hydrogen adsorption [11], the second neighbours are only slightly perturbed. We adjust the s-electron diagonal Hamiltonian elements to keep  $\Delta N_{is} = 0$ . For CO we prefer to exclude the self-interaction [12, 24] and put

$$\epsilon_\sigma = \epsilon_\sigma^0 + U_a(0.5 \Delta N_\sigma + \Delta N_{\pi x} + \Delta N_{\pi y}) \quad (2)$$

$$\epsilon_{\pi x} = \epsilon_{\pi x}^0 + U_a(\Delta N_\sigma + 0.5 \Delta N_{\pi x} + \Delta N_{\pi y}) \quad (3a)$$

$$\epsilon_{\pi y} = \epsilon_{\pi y}^0 + U_a(\Delta N_\sigma + \Delta N_{\pi x} + 0.5 \Delta N_{\pi y}) \quad (3b)$$

The factor 0.5 in the above formulas allows for the interaction of electrons in the same orbital only if they differ in spin. The bare CO levels  $\epsilon_0$  will be discussed later.

Since  $E_F$  is fixed at its bulk value one cannot obviously expect a globally charge-neutral result. There is only a small charge-neutrality violation for CO on M(111) ( $M = \text{Pd, Pt}$ ) whereas at bimetallic surfaces we get usually a charge excess of  $\sim 0.1\text{--}0.3e$ . In calculations [12, 24] a small ad hoc intersite Coulomb parameter was introduced to remove the charging. We chose another method. Let us presume that the size of a particular orbital occupation change, calculated via equations (1)–(3), reflects the orbital's ability to participate in the charge redistribution. This idea motivated us to postulate the corrected orbital occupations  $\Delta N_i^{(2)}$  by putting

$$\Delta N_i^{(2)} = \Delta N_i + \lambda |\Delta N_i| \quad \lambda = - \frac{\sum_I \Delta N_I}{\sum_I |\Delta N_I|}$$

adjusted to restore the global charge neutrality. Note that by omitting the absolute-value operation in the expression for  $\Delta N_i^{(2)}$  one would get the unacceptable solution  $\Delta N_i^{(2)} = 0$ . The Coulomb integrals are now re-evaluated to yield  $\Delta N_i^{(2)}$ . The second self-consistency step leads mainly to some reduction of the  $\pi$  backdonation from the metal to the  $2\pi^*$  states. Numerical tests show that the scheme has a stabilizing effect since it tends to suppress the influence of model parameter variations on the results.

A natural reference level in solid-state calculations is the Fermi energy, not the vacuum level. We align the  $5\sigma$  level to  $E_F$  by writing  $\epsilon_\sigma^0 - E_F = -I_\sigma + \Phi$  where  $I_\sigma = 14$  eV is

the ionization energy of the free-molecule  $5\sigma$  level and  $\Phi$  is the crystal work function. We believe that such a fitting is more reliable than the tendency common in quantum chemistry to extract the input parameters from atomic properties. The fact that the adsorbate 'feels' the work-function value is corroborated by experiments on xenon physisorption [4, 26]. The measurements [2, 3, 27–29] show that  $\Phi$  always grows due to Pt deposition whereas at monolayer Pd coverage there is a small drop. For the HCP substrates Re and Ru we miss the exact values and the situation is further complicated by the scatter of data for the elemental HCP crystals [30, 31]. We put  $\Phi = 5.5$  eV (5.6 eV) for Pd (Pt) overlayer on both substrates; cf. the second issue in [13].

The model is sensitive to the parameter  $\delta = \epsilon_{\pi}^0 - \epsilon_{\sigma}^0$  defining the 'bare'  $2\pi^*$  level. There are experimentally observed  $5\sigma \rightarrow 2\pi^*$  transitions in the gas phase into the singlet (triplet) state with energy 8.07 eV (6.04 eV) [32]. The local-density functional theory gives  $\delta \sim 7$  eV [33, 34] which coincides with the weighted average of the above transitions. In preliminary calculations we have found satisfactory agreement with the available data for CO on elemental metal surfaces for  $\delta = 8.07$  eV and we retain this value. To understand its origin one needs, however, to take the difference [25, 35] between the local potential and Hartree–Fock picture into account. In local potential theories electrons are subject to a common local potential. It is supposed that the local potential stemming from an averaging [25] can avoid the problem of self-interaction. The local potential schemes represent an excellent approximation in many solid-state calculations although some limitations are also documented [36]. Note that for extended systems (solids) the correct formulation of the problem is not clear since the non-local terms depend on the choice of basis employed to construct the wave functions [36]. In the Hartree–Fock method the non-locality arises from projectors introduced to exclude the self-interaction. Hence, if there are  $N$  electrons, the electron in an occupied orbital interacts with  $(N - 1)$  electrons. If the ground-state Hamiltonian is used to evaluate an eigenvalue above  $E_F$ , however, the electron feels all the  $N$  ground-state electrons and the eigenvalue itself is pushed  $\sim U$  (Coulomb parameter) higher than in local schemes. In the present calculations one electron transferred from  $5\sigma$  to  $2\pi^*$  states would be shared by the two  $\{\pi_x, \pi_y\}$  orbitals, i.e. by four spin-orbitals. The bare level  $\epsilon_{\pi}^0$  is thus lowered only by  $\sim U/4$ , as follows from equation (3) if the deviation  $\Delta N_{\sigma} = -1$ ,  $\Delta N_{\pi_x} = \Delta N_{\pi_y} = 0.5$  from the ground-state charge distribution is respected. In local potential schemes with the self-interaction the factor 0.5 in equation (3) would not be present and the correction of the  $\pi$ -level energy would be zero. To get the same left-hand side in equation (3) the bare  $\pi$  level in the theory without self-interaction must lie  $U/4$  higher than in the local theory. Since the local potential guess is  $\delta \sim 7$  eV and the screened Coulomb parameter is  $U_a = 6$  eV we should put  $\delta \gtrsim 8$  eV in accord with the original attempt.

The energy of adsorption  $E_a$  in one-electron theories comprises the change of the electronic energy due to the adsorption and the sum of pairwise repulsive potentials between the adsorbate and its surface neighbours [37]. We shall only be interested in the adsorption energy comparison for geometries with the same CO coordination and with a fixed C–Pd (Pt) distance. The repulsive terms remain unchanged and therefore need not be considered. The change of the electronic energy can be written [24, 38] as

$$\Delta E_{el} = \sum_I \left\{ \int^{E_F} E \Delta n_I(E) dE - \Delta \epsilon_I N_I - 0.5 \Delta \epsilon_I \Delta N_I \right\} \quad (4)$$

where  $n_I(E)$  is the partial LDOS associated with the orbital  $I$ , and  $\epsilon_I$  and  $N_I$  are the Coulomb integrals and occupation numbers respectively (the  $\Delta N_I$  have been denoted above as  $\Delta N_I^{(2)}$  during the self-consistency discussion). The integral in equation (4) describes the

change of the so-called band energy and the following two terms compensate for the double counting of the Coulomb energy [24, 38]. The band-energy changes due to the metal s electrons are very small and since the s-electron description is simplified in our model, we do not include this contribution in the final results. It might seem that subtraction of doubly counted Coulomb interaction is a poorly defined attempt because, e.g., of the uncertainty in Coulomb parameters  $U$ . Fortunately, whatever the self-consistency prescription be, the changes in  $\Delta E_{el}$  cancel up to the second order in  $\Delta\epsilon_I$  showing a kind of invariance in the expression (4) that makes the model stable. To the first order in the  $\Delta\epsilon_I$  this result has been derived in [39, 40]. The proof of its present generalization follows the analysis of [39]. It is also correct when the paramagnetic state is not assumed and the spin index appears in the multi-index  $I$ . It is convenient to introduce the notation  $z = E + i0$ ,  $J(\cdot) = -\pi^{-1}\text{Im}(\cdot)$ . For the Green-function matrix (resolvent)  $G = G(z)$ ,  $n_I(E) = J(\langle I|G(z)|I\rangle)$  holds. Defining  $\Delta\epsilon$  as a diagonal matrix with elements  $\Delta\epsilon_I$  the perturbation expansion up to the second order reads

$$\sum_I \Delta n_I(E) = J[\text{Tr}(G \Delta\epsilon G + G \Delta\epsilon G \Delta\epsilon G)].$$

The trace is taken over the part of the crystal where the perturbation cannot be neglected. Because of the cyclic invariance of the trace and the identity  $G^2 = -dG/dz$  the expression is brought into the form  $dX/dz$  with  $X = -J[\text{Tr}(G \Delta\epsilon + 0.5G \Delta\epsilon G \Delta\epsilon)]$ . This leads to the relation

$$X(E_F + i0) = \sum_I \int^{E_F} \Delta n_I dE = \sum_I \Delta N_I$$

that will be used later. To evaluate the change of the band energy one has to integrate  $z dX/dz = -X + d(zX)/dz$ .  $\int^{E_F} (-X) dE$  cancels mutually with the remaining terms in (4) to the second order in  $\Delta\epsilon$ . Integration of  $d(zX)/dz$  gives

$$E_F X(E_F + i0) = E_F \sum_I \Delta N_I$$

which is zero because of the charge conservation.

Core-level shifts have a crucial role at bimetallic surfaces [2]. For a long time two simplified theories, the initial-state picture and the  $Z+1$  (or equivalent-core) approximation were widely used in CLS studies [4]. Recent progress in the field shows (for elemental metal surfaces, at least) that the correct values lie halfway between the two values predicted by the above approximations [41] but error introduced by either of the approximations is not large ( $\lesssim 0.2$  eV) [42]. As in [5–7, 11, 13] we employ a simplified initial-state theory supposing that in transition-metal atoms the core electrons feel a potential change analogous to that experienced by compact d electrons. This means simply that  $\Delta\text{CLS} = -\Delta\epsilon_I$ ,  $I = (i, d)$ . Our calculations for Pd overlayers [5–7, 11] yield the correct CLS sign but for a heavily strained (stressed) epitaxial monolayer at Ta(110) (Ru(0001)) our values are clearly underestimated (overestimated) when compared with experiments. The theoretical investigation for Pd/Nb(110) [15] indicated that our interface Pd–Ta separation should have been a bit further reduced which results in an improvement by 0.1 eV: we get for the Pd/Ta(110) surface a CLS of 0.3 eV as compared with the Pd(111) surface. We have verified, however, that this bond shortening has practically no effect on the results on CO adsorption and we use the old parameters [5, 6]. However, we suspect [7] that the main cause of the discrepancy is the canonical scaling  $R^{-q}$ ,  $q = 5$ , of the Pd–Pd hopping elements with the distance  $R$ . If a smaller  $q$  were used the CLS predictions would be more accurate. If this is the case, the CO adsorption energy as it is presented below for Pd/Ta(110) (Pd/Ru(0001)) is somewhat overestimated (underestimated).

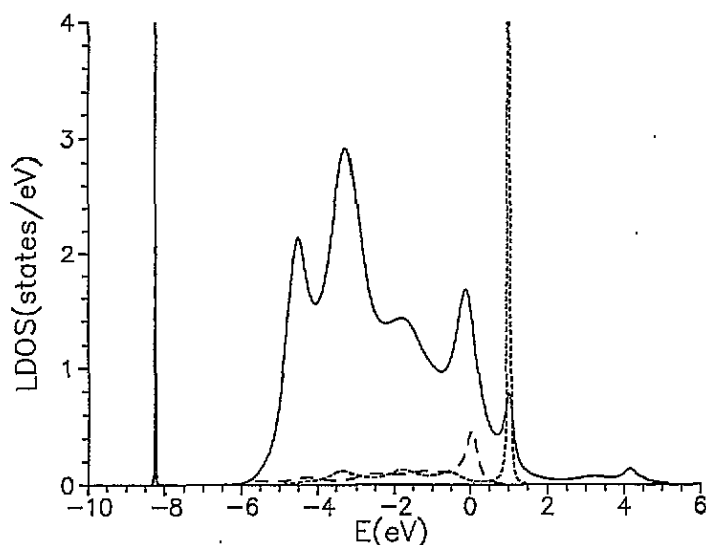


Figure 1. The local density of electronic states (LDOS) for an isolated CO molecule at the atop site above Pd(111) for the CO metallic nearest-neighbour d electrons (full line), the molecule  $5\sigma$  states (long-dashed line) and  $2\pi^*$  states (short-dashed line) states, respectively.  $E_F$  coincides with the energy zero.

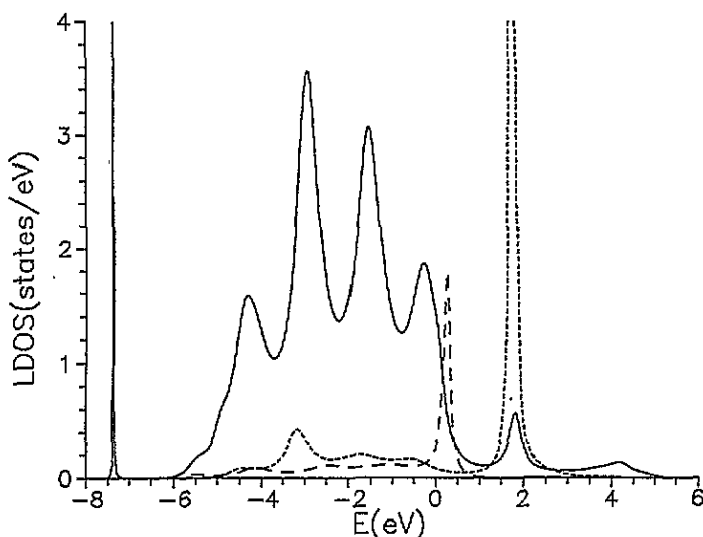


Figure 2. As figure 1 but for the adsorption at the hollow FCC-like site.

### 3. Results and discussion

Let us start with the CO chemisorption above the elemental metal surfaces. We show LDOS for the CO at atop and hollow sites, respectively, above Pd(111) in figures 1 and 2; for Pt(111) the LDOS behaviour is qualitatively analogous. The LDOS for the bridge adsorption is much like that in the hollow case. Further details concerning the adsorption are given in tables 1 and 2. The photoemission signal from late transition metals is enhanced due to a CO presence below the centre of the d band (4–5 eV below  $E_F$  for Pt [43]) at the cost

of states at  $E_F$ . The effect is apparent (peak at about  $-3$  eV) in our figures. The position of the occupied  $5\sigma$  peak we found corresponds reasonably with experiments [1]. Note that an exact agreement is not obtained in other models of similar systems either [34, 44, 45]. The reason of small discrepancies could be the sensitivity of the result to the C–O bond-length variation [45] or a final-state effect. Extended Hückel calculations [21, 46] place the feature too close to  $E_F$ . The antibonding partially occupied peak at  $E_F$  originating from the molecule  $5\sigma$  states is an indication of the  $\sigma$  bonding; a similar feature has been found in [44]. We find the empty  $2\pi^*$  peak considerably closer to  $E_F$  than revealed by the inverse photoemission [47]. Since other authors [21, 45] do not reproduce the exact position either one can speculate that the cause could be an incomplete screening of the extra electron in the experiment. The occupied bonding  $\pi$  states are smeared over a considerable energy range. The magnitude  $\Delta N_\pi$  of the  $\pi$  backdonation in tables 1 and 2 is similar to that in the model [34] of CO at Co(0001). Our  $\sigma$ -donation predictions differ from the trend in [34] by a reduction of  $\Delta N_\sigma$  when going to the atop site above Pd(111).

**Table 1.** Selected results of calculation for an isolated CO molecule at the atop (1), bridge (2) and hollow (3) sites at Pd and Pd/M (M = Ta, W, Re and Ru) surfaces.  $-\epsilon_\sigma$  is the position of the  $5\sigma$  peak below  $E_F$ ,  $\Delta N_\sigma$  ( $\Delta N_\pi$ ) is the change of the  $5\sigma$  ( $2\pi^*$ ) orbital occupation,  $\Delta E_a$  is the change of the chemisorption energy as compared to that of the analogous adsorption site at Pd(111).  $\Delta$ CLS is the additional core-level shift induced by the chemisorption at the metal nearest neighbour(s) of CO. CLSs on nonequivalent CO neighbours at the hollow site above the BCC substrates differ by less than 0.05 eV. Pd<sub>i</sub>/Ta(110) stands for the hexagonal incommensurate Pd overlayer.

System	Site	$-\epsilon_\sigma$ (eV)	$\Delta N_\sigma$	$\Delta N_\pi$	$\Delta E_a$ (eV)	$\Delta$ CLS (eV)
Pd(111)	1	8.3	-0.13	0.37	0.0	0.9
Pd/Ta(110)	1	8.7	-0.07	0.37	0.1	0.7
Pd <sub>i</sub> /Ta(110)	1	9.0	-0.05	0.31	-0.1	0.5
Pd/W(110)	1	8.8	-0.07	0.31	-0.1	0.5
Pd/Re(0001)	1	8.7	-0.08	0.37	0.0	0.7
Pd/Ru(0001)	1	8.7	-0.08	0.32	0.0	0.7
Pd(111)	2	7.8	-0.39	0.80	0.0	0.7
Pd/Ta(110)	2	7.7	-0.06	0.42	-0.6	0.2
Pd <sub>i</sub> /Ta(110)	2	7.1	-0.04	0.39	-0.7	0.1
Pd/W(110)	2	7.7	-0.07	0.37	-0.8	0.2
Pd/Re(0001)	2	8.2	-0.16	0.49	-0.5	0.4
Pd/Ru(0001)	2	8.2	-0.18	0.50	-0.5	0.4
Pd(111)	3	7.4	-0.45	0.82	0.0	0.4
Pd/Ta(110)	3	7.9	-0.07	0.43	-0.4	0.1
Pd <sub>i</sub> /Ta(110)	3	8.4	-0.08	0.41	-0.8	0.1
Pd/W(110)	3	8.1	-0.08	0.37	-0.6	0.5
Pd/Re(0001)	3	7.9	-0.15	0.45	-0.4	0.2
Pd/Ru(0001)	3	8.0	-0.17	0.46	-0.5	0.2

To illustrate the situation at bimetallic interfaces we present the LDOS for CO at Pd/Ta(110) in figures 3 and 4 (cf. [13] for some other systems) and general results in tables 1 and 2. At the hollow and bridge site the  $\sigma$  donation and especially the  $\pi$  backdonation are significantly lower than at the corresponding elemental metal surface. The conclusion agrees with [28] whereas in the model [46] the change of the backdonation is stressed. The trend correlates with a weakening of the CO overlayer bond. The Pd LDOS is not seriously affected by CO in the hollow position above Pd/Ta(110) as seen from a comparison of figure 4 with [6]. For the atop position the weakening is much less marked. We even come to a



Table 2. As table 1 but for Pt overlayers.

System	Site	$-\epsilon_\sigma$ (eV)	$\Delta N_\sigma$	$\Delta N_\pi$	$\Delta E_\sigma$ (eV)	$\Delta\text{CLS}$ (eV)
Pt(111)	1	9.1	-0.21	0.49	0.0	1.2
Pt/Ta(110)	1	9.6	-0.10	0.38	-0.5	0.8
Pt/W(110)	1	9.5	-0.12	0.34	-0.3	0.7
Pt/Re(0001)	1	9.5	-0.13	0.40	-0.1	0.8
Pt/Ru(0001)	1	9.6	-0.12	0.35	-0.3	0.7
Pt(111)	2	8.0	-0.14	0.37	0.0	0.2
Pt/Ta(110)	2	7.4	-0.05	0.30	-0.2	0.1
Pt/W(110)	2	7.6	-0.06	0.22	-0.4	0.1
Pt/Re(0001)	2	8.1	-0.07	0.29	-0.2	0.2
Pt/Ru(0001)	2	8.3	-0.09	0.26	-0.4	0.2

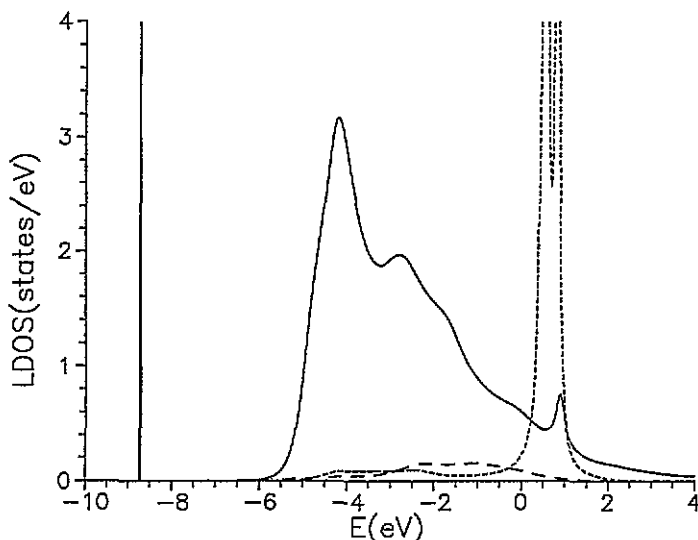


Figure 3. As figure 1 but for the atop site above the epitaxial Pd monolayer on Ta(110).

stabilization of atop CO above the epitaxial monolayer Pd/Ta(110). This could be an artifact due to the distance dependence of matrix elements discussed in the preceding section but the overall trend should be correct. The differences that we find between the commensurate and incommensurate Pd films over Ta(110) (table 1) are not large, in agreement with measurements [48]. The large difference between the atop and more coordinated sites suggests that in some Pd overlayers the atop site might become favoured. The magnitude of the energetic advantage of the threefold site over the atop position at Pd(111) is not known reliably. An evaluation causes trouble even in first-principles methods [49]; the semi-empirical models [21, 50] yield  $\sim 0.6$  eV. Hence, Ta and W(110) substrates are likely candidates (table 1) for the preferred adsorption site change. This speculation agrees with the conclusions drawn from the vibrational spectra for CO on Pd/Ta(110) [48, 51]. For the remaining systems a similar analysis is lacking; the model in [46] prefers the hollow site at Pd/W(110) very slightly. The above discussion together with table 1 suggest that CO should be less stable by about 0.6 eV at Pd/Ta(110) than at Pd(111) in accordance with measurements [48, 51]. For other Pd layers we predict a CO surface bond weakening in agreement with the experimentally observed trend [2, 3, 27–29]. For Pt overlayers an

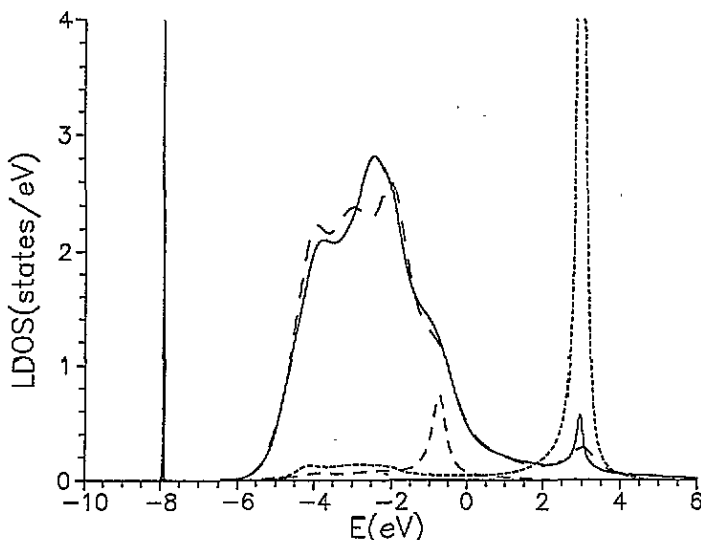


Figure 4. As figure 1 but for the threefold hollow site above the epitaxial Pd monolayer on Ta(110). Since the three Pd neighbours of CO are not equivalent, the d-electron LDOS for the pair of two equivalent atoms is represented by the longest-dashed line.

analogous tendency is also indicated [3, 52].

Originally [13] we were sceptical about the simple local nature of CO behaviour. Having analysed additional data we now believe that a lucid explanation of gross trends exists. To elucidate the chemisorption at extended surfaces the concept of the group orbital localized on the surface atoms close to the adsorbate is often used [34]. Let us suppose that the pair  $(\pi_x, \pi_y)$  of the  $2\pi^*$  is the right LUMO choice [21]. For the atop adsorption the metal HOMO is simply an atomic orbital whereas for the hollow (bridge) site it resides on three (two) surface atoms. Elementary geometric considerations [21] show that, because of the antisymmetry of the molecular  $\pi$  orbitals, a delocalized antisymmetric group orbital has an antibonding character. Hence, the energy of LUMO for the threefold and twofold sites lies higher, i.e. closer to  $E_F$  than for the atop site. Therefore the  $\pi$  backdonation and the bond are generally stronger for multiply coordinated sites. On the other hand, the Pd(Pt) overlayer LDOS below  $E_F$  is depleted due to interaction with the another metal substrate [2, 3] and it is not surprising that the atop-site HOMO is less perturbed thus explaining the small changes we find for this site. It is interesting that a switch from the atop to the hollow site for CO at Ru(0001) induced by Cs co-adsorption has been observed experimentally [53]. It would be interesting to consider the effect from the above point of view.

We can corroborate the previous reasoning by numerical data. Let us denote by  $|0\rangle$  one of the three  $\sigma, \pi_x, \pi_y$  CO orbitals considered in our model. Starting from  $|0\rangle$  another orbital

$$|1\rangle = b^{-1}(H|0\rangle - a|0\rangle) \quad (5)$$

is constructed in the recursion method [54]. Above,  $H$  is the Hamiltonian,  $a$  assures the orthogonality of the two vectors and  $b^{-1}$  is the normalization constant. Let us prove that  $|1\rangle$  makes the matrix element  $h = \langle 1|H|0\rangle$  extremal. We employ the variational principle  $\delta(h - \lambda_1 c_1 - \lambda_2 c_2) = 0$ , where  $\lambda_{1,2}$  are the Lagrange multipliers appearing because of the conditions  $c_1 = \langle 1|0\rangle = 0$ ,  $c_2 = \langle 1|1\rangle = 1$ . If the orbitals are real  $\delta\langle 1|1\rangle = 2\langle \delta(1)|1\rangle$  and the resulting equation  $H|0\rangle - \lambda_1|0\rangle - 2\lambda_2|1\rangle = 0$  is equivalent to the definition (5). Hence,  $|1\rangle$  is an appropriate choice of the group orbital. In table 3 we give the calculated energies

of the group orbital  $\epsilon(\alpha) = \langle 1|H|1 \rangle$  with  $|0\rangle = |\alpha\rangle$ ,  $\alpha = \sigma, \pi$  for various adsorption sites above Pd layers. At BCC surfaces the two  $\pi$  orbitals are not equivalent and we take the average energy. We also include the group orbital associated with the  $5\sigma$  orbital into the table 3 orbital since the  $5\sigma$  level becomes slightly depopulated. For the atop adsorption the correlation between the HOMO shifts and adsorption energy variation is not convincing. The reason is that the energy changes are small and other factors, such as the minor changes of the local geometry or work function, can have a role. For the bridge and hollow positions where rather large  $\Delta E_a$  are frequent the correlation is quite good, especially if the  $\pi$  interaction is considered. For Pt the situation is similar.

**Table 3.** The metal group orbital energy  $\epsilon(\alpha)$ ,  $\alpha = \sigma, \pi$  with respect to the Fermi level  $E_F$  is compared with the adsorption energy  $\Delta E_a$  change. The atop (1), bridge (2) and hollow (3) adsorption site and the case of Pd overlayers is considered. Pd<sub>i</sub> is the incommensurate Pd overlayer. See the text for details.

System	Site	$\epsilon(\sigma)$ (eV)	$\epsilon(\pi)$ (eV)	$\Delta E_a$ (eV)
Pd(111)	1	-2.6	-2.7	0.0
Pd/Ta(110)	1	-2.8	-2.9	0.1
Pd <sub>i</sub> /Ta(110)	1	-2.8	-2.8	-0.1
Pd/W(110)	1	-2.9	-3.0	-0.1
Pd/Re(0001)	1	-2.8	-2.8	0.0
Pd/Ru(0001)	1	-2.9	-2.9	0.0
Pd(111)	2	-2.8	-2.4	0.0
Pd/Ta(110)	2	-2.6	-2.5	-0.6
Pd <sub>i</sub> /Ta(110)	2	-2.4	-2.3	-0.7
Pd/W(110)	2	-2.8	-2.8	-0.8
Pd/Re(0001)	2	-2.9	-2.5	-0.5
Pd/Ru(0001)	2	-3.0	-2.6	-0.5
Pd(111)	3	-2.7	-2.1	0.0
Pd/Ta(110)	3	-2.9	-2.4	-0.4
Pd <sub>i</sub> /Ta(110)	3	-3.1	-2.2	-0.8
Pd/W(110)	3	-3.2	-2.5	-0.6
Pd/Re(0001)	3	-3.0	-2.3	-0.4
Pd/Ru(0001)	3	-3.1	-2.4	-0.5

The HOMO energies reflect both the variation of atomic Coulomb integrals  $\epsilon_I$  and the local geometry. Since the Coulomb-integral change is up to the sign equal to CLS in the initial-state picture it is natural that atoms with more positive CLS bind CO less [2]. Let us note, however, that the HOMO energies in table 3 contain the self-consistent corrections (i.e.  $\Delta$ CLS from table 1) due to the CO adsorption whereas in [2] the CLS at adsorbate-free overlayers are systematically studied.

The last point we touch upon is the additional CLS change  $\Delta$ CLS induced by the molecule on adjacent metallic atoms. Tables 1 and 2 show that the calculated  $\Delta$ CLS are always positive and are smaller at more coordinated sites. The sign and order of the magnitude agree with the published measurements for late transition metals [4, 55, 56]. Unfortunately we have not found results for Pd(111) or Pt(111). Information on the influence of local geometry is also scarce [57]. For several bimetallic systems we consider that the  $\Delta$ CLS are known [27]. Our result for Pd/Re(0001) is close to the experimental value 0.6 eV if the hollow adsorption site is assumed. For the hollow (atop) chemisorption site above Pd/Ru(0001) (Pd/Ta(110)) our guess is somewhat of an underestimate (overestimate). Again this could be partly due to the uncertainty in the matrix elements scaling if the covalent

radii of the two metal differ substantially.

To summarize, we get semiquantitative accord with a number of experimental data for CO chemisorption above Pd monolayer grown on differing substrates. The gross trends in the chemisorption are related to the energy of the palladium group orbital (HOMO) interacting with the molecule  $2\pi^*$  (LUMO) level. Particularly, the change of the adsorption site observed for Pd/Ta(110) can be anticipated. The change of the calculated core-level shift induced by the molecule at adjacent metal atoms decreases generally with the CO coordination. Verification of this prediction might be extremely useful in further investigations.

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