

CO adsorption on the Pt(1 1 1) surface: a comparison of a gradient corrected functional and a hybrid functional

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Abstract

The adsorption of CO on the Pt(1 1 1) surface in a ($\sqrt{3} \times \sqrt{3}$) pattern has been studied with the gradient corrected functional of Perdew and Wang and the B3LYP hybrid functional. A slab which is periodic in two dimensions is used to model the system. The Perdew–Wang functional incorrectly gives the fcc site as the most favorable adsorption site, in accord with a set of previous studies. The B3LYP functional gives the top site as the preferred site. This confirms results from cluster studies where it was suggested that the different splitting, dependent on the functional, between highest occupied and lowest unoccupied molecular orbital, could be the reason for this change of the adsorption site. This is supported by an analysis based on the projected density of states and the Mulliken population.

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1. Introduction

The adsorption of CO on the Pt(1 1 1) surface is of enormous importance in materials science, because of the high economical and environmental implications. This process is not at all simple and still poses challenges to experimentalists and theoreticians. Especially the question of the site which

is occupied by the CO molecule has triggered a huge interest in the community of those performing ab initio calculations.

Experimentally, it is well established that the top site is occupied at this coverage, and there is also a minority of bridge sites occupied (see, e.g., Refs. [1,2], with low energy electron diffraction and electron-energy-loss spectroscopy, reflection–absorption spectroscopy [3] or the scanning tunneling microscopy experiments [4] which were interpreted [5] in such a way that they should display CO in top and bridge sites).

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First principles density functional calculations, however, lead to a different result: as was summarized in Ref. [6], well converged calculations favor the high coordination sites, and they found that the fcc (face centered cubic) hollow site was lowest in energy. This was obtained with local-density or generalized gradient exchange correlation potentials, and with various codes. No conclusive reason for this failure of the density functional calculations could be given. The article initiated further studies, and in some of them, the top site was found to be lowest in energy: it was argued that the inclusion of relativistic effects should lead to the correct adsorption site [7,8]. Others [9] confirmed the wrong site preference with the top site higher in energy, although a relativistic pseudopotential was used. They argued that the failure was because different bond orders were treated with varying accuracy due to the generalized gradient approximation. A similar argument was that the error could be due to the incorrect description of the HOMO–LUMO gap (difference between highest occupied and lowest unoccupied molecular orbital), due to the functional employed [10,11], and the different occupancy of the orbitals, depending on the adsorption site. This analysis was based on cluster calculations and calculations with a gradient corrected functional for the periodic system. The authors suggested to use hybrid functionals [10] or methods such as LDA + U [11] to obtain a better description of the HOMO–LUMO gap.

Therefore, there are several reasons to study this system: Most important is that the code used allows to employ hybrid functionals for periodic systems so that the impact of these functionals, which include Fock exchange, can be tested. It thus makes it possible to test the suggestion [10] that hybrid functionals might lead to a preference of the top site. Note that this suggestion was based on a cluster model, and only by an extrapolation it could be argued that the top site would be preferred with a hybrid functional. It is therefore interesting to perform calculations on the periodic system and thus to remove the necessity of a cluster approximation and the extrapolation. As a side effect, the approach used here is based on local orbitals instead of plane waves, so that a somewhat different technique is used, and a comparison with the plane

wave results for the slab calculations with the gradient corrected functional is possible.

The article is structured as follows: after defining the computational parameters and the slab model used, Pt bulk, the clean Pt(111) surface, and the CO adsorption on the Pt(111) surface are studied. This is done with a gradient corrected and a hybrid functional, for comparison. The focus is on the coverage of one third of a monolayer, in a ($\sqrt{3} \times \sqrt{3}$) adsorption pattern. Finally, the results are discussed and summarized.

2. Computational parameters

2.1. Basis set and method

A local basis set formalism was used where the basis functions are Gaussian type orbitals centered at the atoms as implemented in the code CRYSTAL03 [12]. For Pt in the slab models, a scalar-relativistic pseudopotential with 18 valence electrons was used [13]. The innermost [2s3p1d] basis functions were kept fixed as in the original basis set [13], in addition one more s-shell (exponent 0.59), one sp-shell (exponent 0.11) and one d-shell (exponent 0.167) were optimized, resulting in a [4s4p2d] basis set as a whole. For the calculations on the free Pt atom, which are necessary to compute the bulk cohesive energy, the original Pt basis set was used [13]. For carbon, the basis set from Ref. [14] was chosen, with the outermost sp-shell (0.26) replaced by two sp-shells (0.40, 0.20), i.e. [4s3p1d] as a whole. Finally, the oxygen basis set from Ref. [15] was chosen, with outermost sp-exponents 0.5, 0.25, 0.1 (instead of 0.45, 0.15) and one d-exponent (0.8), i.e. [5s4p1d]. The basis sets are displayed in Table 1. The numerical integration of the density functional energy was performed on a grid, without fitting the potential with the help of an auxiliary basis set as it had to be done with the CRYSTAL98 code.

Two functionals were used: the gradient corrected functional of Perdew and Wang (PW91) [16], and the hybrid functional B3LYP. The CRYSTAL03 code [12] was used for all the calculations, except for the calculations of the free Pt atom where the Molpro2002 code [17] was used.

Table 1
The Gaussian basis sets used

	Pseudopotential [13]	
	Exponent	Contraction
<i>Pt 1s, 2sp, 3spd, 4spdf</i>		
5s	16.5595630	−0.8849447
	13.8924400	1.5011228
	5.8536080	−1.5529012
6s	1.2873200	1.0
7s	0.59	1.0
8s	0.11	1.0
5p	7.9251750	4.9530757
	7.3415380	−5.8982100
	1.9125150	0.3047425
	1.0715450	0.7164894
7p	0.4379170	1.0
8p	0.11	1.0
5d	3.9395310	−0.5826439
	3.5877770	0.5922576
	1.2862310	0.4736921
	0.5198140	0.5765202
6d	0.167	1.0
<i>C</i>		
1s	as in [14]	
2sp	3.665	s: −0.3959 p: 0.2365
	0.7705	s: 1.216 p: 0.8606
3sp	0.40	s: 1.0 p: 1.0
4sp	0.20	s: 1.0 p: 1.0
3d	0.8	1.0
<i>O</i>		
1s	as in [15]	
2sp	49.43	s: −0.00883 p: 0.00958
	10.47	s: −0.0915 p: 0.0696
	3.235	s: −0.0402 p: 0.2065
	1.217	s: 0.379 p: 0.347
3sp	0.500	s: 1.0 p: 1.0
4sp	0.250	s: 1.0 p: 1.0
5sp	0.10	s: 1.0 p: 1.0
3d	0.8	1.0

2.2. Slab model

The adsorption was modeled by using a five-layer platinum slab with the platinum atoms arranged as in the face-centered cubic lattice, at the PW91 (and B3LYP)-optimized bulk Pt lattice constant of 4.01 Å (and 4.05 Å). CO was adsorbed on one side of this slab, vertical to the (111) surface. A supercell approach with a $(\sqrt{3} \times \sqrt{3})$ adsorption pattern as in the experiment was used. This slab was not repeated in the third dimension so that the model is truly two-dimensional (see Fig. 1).

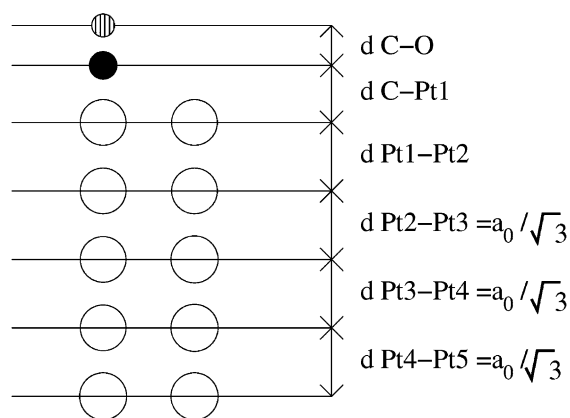


Fig. 1. Definition of the geometrical parameters of the slab model. All distances are interlayer distances.

Four adsorption sites were considered (see Fig. 2): the top adsorption site with CO sitting vertically above a platinum atom in the top layer, the bridge site with CO sitting above the middle of two Pt atoms in the top layer, and two different threefold hollow sites where the CO molecule is

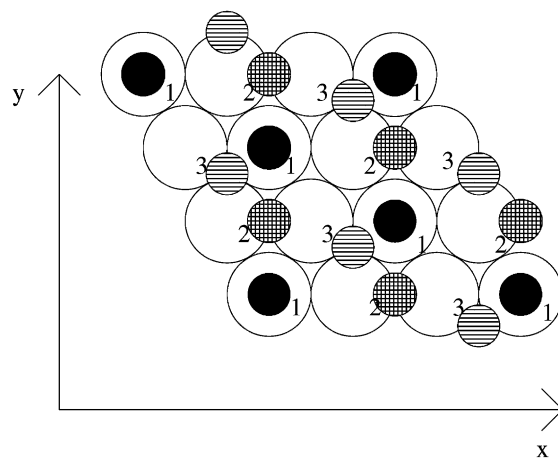


Fig. 2. The structures considered for CO, adsorbed on the Pt(111) surface, at a coverage of one third of a monolayer, $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell. The platinum atoms in the top layer are displayed by open circles. The considered CO adsorption sites are the top site above the Pt atoms with number 1 (filled circles), the threefold hollow sites above atoms 1,2,3 (fcc or hcp hollow, circles with horizontal lines) or the bridge site above atoms 2 and 3 (circles with horizontal and vertical lines). Note that the threefold hollow sites cannot be distinguished in this figure.

placed vertically above a platinum atom in the second (third) platinum layer. The first of the threefold hollow sites is referred to as the hcp (hexagonal close-packed) hollow site because the CO molecule is vertically above a platinum atom in the second Pt layer. The second of the threefold hollow sites is referred to as the fcc hollow site because the CO molecule is vertically above third layer Pt atoms.

For comparison, the vertical relaxation of the platinum atoms was simulated in two different ways for the top site: simulations were performed where only a uniform relaxation of the top platinum layer was possible, and simulations where a different vertical relaxation for the platinum atoms in the top layer was possible (i.e. substrate rumpling). This was done for the top site where this effect is expected to be most important [18,19]. This led however, to only a very small change in the binding energy and is thus negligible. Also, for the hcp site, a possible second layer rumpling was considered, i.e. the Pt atom vertically under the CO molecule in the second Pt layer was allowed to relax. This led to an even smaller change and thus is also considered negligible.

A \vec{k} -point sampling net of the size $16 \times 16 \times 16$ for the bulk and 16×16 for the surfaces was used. The Fermi function was smeared with a temperature of $0.01 E_h$ ($1 E_h = 27.2114 \text{ eV}$) to make the integration numerically more stable.

2.3. Pt bulk and (111) surface

The results for Pt bulk and the Pt(111) surface are summarized in Tables 2 and 3. The lattice constant is slightly overestimated with both func-

Table 3
The surface energy of the Pt(111) surface.

Method	Relaxation of the top layer (Å)	Surface energy $\frac{E_h}{\text{Surface atom}}$
PW91	Disallowed	0.025
PW91	0.05	0.024
B3LYP	Disallowed	0.020
B3LYP	0.05	0.019
Ref. [29], PW91	0.023	0.021
Exp., Ref. [30]	0.025 ± 0.01	

tionals. The cohesive energy (with respect to the free atom in its d^9s^1 ground state) is slightly underestimated with the PW91 functional, and even more with the B3LYP functional. The fact that B3LYP underbinds can be attributed to the admixture of Fock exchange, and the fact that Hartree–Fock usually underbinds, especially for metals. This was already observed, for example, in B3LYP calculations for silver [20].

The Pt(111) surface relaxes outwards, which is different from other metals, for example copper or silver. This is, however, consistent with the finding that the Mulliken charge is slightly larger in the outermost layer ($78.05 |e|$, i.e. $-0.05 |e|$). This is in contrast to Cu(111) and Ag(111), which relax slightly inwards, and where the Mulliken charge is slightly positive in the outermost layer (copper [21]: $28.97 |e|$, i.e. $+0.03 |e|$; silver [22]: $46.98 |e|$, i.e. $+0.02 |e|$). Thus, if the atoms were considered as spheres with a radius dependent on the charge, then the outwards relaxation of Pt (and inwards relaxation of Cu and Ag) would be consistent with the Mulliken charge.

2.4. CO adsorption

The results of the optimizations of the CO adsorption on the Pt(111) surface are displayed in Table 4. First, we note that the PW91 functional gives the wrong site preference: in agreement with most of the previous studies, the fcc hollow site is preferred, by $0.0037 E_h$, when comparing to the top site. This result is in good agreement with previous calculations [6] where it was computed to be 0.10 or 0.23 eV ($0.0037 E_h$ or $0.0085 E_h$), depending on the method and code used. Thus, with the scalar-relativistic pseudopotential used in the present

Table 2
The ground state properties of bulk Pt

	Lattice constant a_0 (Å)	E_{coh} (E_h)	B (GPa)
PW91, this work	4.01	0.192	227
B3LYP, this work	4.05	0.138	234
Ref. [26], LDA	3.92	0.276	310
Ref. [26], PBE	3.99	0.248	270
Ref. [27], LDA	3.90	–	307
Ref. [27], PW91	3.97	–	246
Exp., Ref. [28]	3.92	0.215	278

Table 4
Adsorption of CO on the Pt(111) surface, PW91 and B3LYP results

Site	$d_{\text{C-O}}$ (Å)	$d_{\text{C-Pt1}}$ (Å)	$d_{\text{Pt1-Pt2}}$ (Å)	$E_{\text{adsorption}}^{E_{\text{h}}}$ [CO molecule]
PW91				
Hcp hollow	1.19	1.38	2.40	−0.0631
Fcc hollow	1.19	1.37	2.40	−0.0639
Bridge	1.18	1.49	2.39	−0.0615
Top	1.16	1.87	2.38	−0.0602
B3LYP				
Hcp hollow	1.18	1.35	2.45	−0.0494
Fcc hollow	1.18	1.33	2.43	−0.0515
Bridge	1.17	1.46	2.43	−0.0506
Top	1.15	1.86	2.39	−0.0531

Five platinum layers are used, of which four have been fixed at bulk positions, i.e. the distances $d_{\text{Pt2-Pt3}}$, $d_{\text{Pt3-Pt4}}$, $d_{\text{Pt4-Pt5}}$ are fixed at $a_0/\sqrt{3} = 2.32$ Å (PW91) or 2.34 Å (B3LYP). The top-most Pt layer is allowed to relax. $d_{\text{C-O}}$ is the distance between carbon and oxygen atom, $d_{\text{C-Pt1}}$ is the distance between the carbon atom and top Pt layer, $d_{\text{Pt1-Pt2}}$ the distance between first and second platinum layer. The adsorption energy is the difference $E_{\text{CO at Pt(111)}} - E_{\text{Pt(111)}} - E_{\text{CO}}$.

study, it could not be confirmed that relativistic effects should change the site preference. The order of the sites is fcc, hcp, bridge, top, i.e. a higher coordination number is favorable, however, the energy splitting is not too large. In all cases, the outermost Pt layer relaxes slightly outwards by 0.06–0.08 Å. In the case of the top site, an additional vertical rumpling was allowed, i.e. the Pt atom vertically below the CO molecule was allowed to relax different than the other two Pt atoms in the top layer. This led, however, to only a marginal change: instead of 0.06 Å like the other two atoms, this third atom relaxed outwards by 0.08 Å. The energy was lowered by 0.0003 E_{h} , i.e. this did not influence the site preference. Also, for the hcp site, the Pt atom in the second layer vertically under the CO was allowed to relax differently (the Pt atoms in the first layer are fixed by symmetry). However, this also resulted in a minor change only (by 0.004 Å, away from CO, i.e. downwards), and the energy did virtually not change. Therefore, in the B3LYP study (which is more time consuming than PW91), only a uniform relaxation of the top layer was performed.

In the following, the B3LYP results are summarized. In the case of this hybrid functional, the top

site has become the preferred site: it is now lowest in energy, the fcc site is higher by 0.0016 E_{h} , the bridge site by 0.0025 E_{h} , and the hcp site by 0.0037 E_{h} . The order of the sites is now top, fcc, bridge, hcp, i.e. the lower coordination sites are more favorable in B3LYP than in PW91.

It was argued that the difference between PW91 and B3LYP was the higher HOMO–LUMO gap which should lead to different binding energies, depending on the site [10,11]. According to the Blyholder model [23], it is thought that the CO 5 σ orbital donates charge to the Pt surface, and charge is back donated to the 2 π^* orbital. Thus the HOMO–LUMO gap, and the position of the HOMO and LUMO with respect to the Fermi energy, are the quantity to look at. For the fcc site, the back donation is larger than for the top site ([10] and this work). The HOMO–LUMO gap is smaller in PW91, and HOMO and LUMO are closer to the Fermi energy in PW91. Thus donation and back donation is energetically more favorable with the PW91 functional, and less favorable with the B3LYP functional where the gap is larger and HOMO and LUMO are lower and higher with respect to the Fermi energy. This argument was presented in Ref. [10] and would explain that the high coordinated sites with a larger back donation are preferred in PW91, but not in B3LYP.

The aforementioned analysis [10] was based on a molecular system, and for the largest cluster considered with the B3LYP functional (Pt₁₈–CO), the fcc site was still more favorable than the top site, although the energy difference between fcc and top site was smaller than with the PW91 functional. By means of an extrapolation, using the PW91 data as a function of the cluster size and PW91 calculations for a slab model, the authors argued that in the limit of a very large cluster or a slab, B3LYP should favor the top site. It is therefore very interesting to study this system with a periodic code and thus to test this extrapolation. Computing the Fock exchange seems still to be easier with codes based on Gaussian type orbitals and not with plane wave codes, and therefore the CRYSTAL03 code is probably the method of choice for this system. In Fig. 3, the density of states (DOS) of the CO overlayer is displayed for

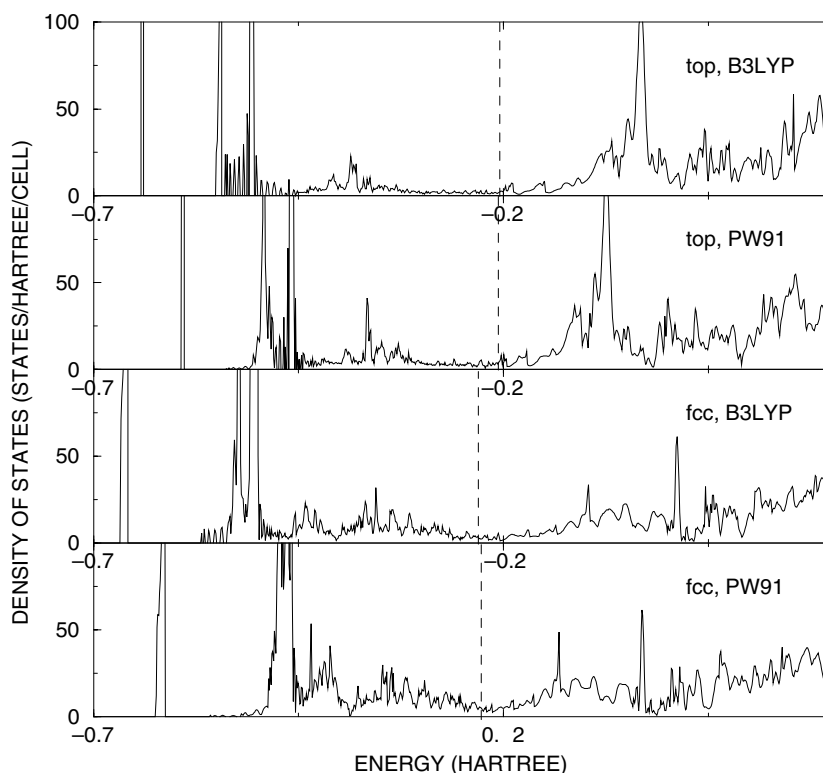


Fig. 3. Density of states, on CO projected, for fcc and top site, and PW91 and B3LYP functional. The Fermi energy is indicated with dashed lines.

the top site and the fcc site, with PW91 and B3LYP, and the orbital projected density of states is displayed in Figs. 4 and 5, for the top site and both functionals. The gap between the peaks in occupied and unoccupied states is clearly larger with the B3LYP functional, in agreement with the cluster study [10]. For example, for the top site, the gap between the peak in the DOS closest to the Fermi energy, and the first peak above the Fermi energy is about $0.48 E_h$ in B3LYP, but only $0.38 E_h$ in PW91, i.e. the gap is larger by about $0.1 E_h$ in B3LYP. In Ref. [10], the gap between 5σ and $2\pi^*$ orbital was determined to be 6.8 eV ($0.25 E_h$) in PW91, and 9.5 eV ($0.35 E_h$) in B3LYP, for an isolated CO molecule. In the present study, the gaps are $0.42 E_h$ in PW91, and $0.51 E_h$ in B3LYP, for the CO molecule adsorbed on the platinum surface, at the top site (the 5σ orbital corresponds to the second peak below the

Fermi energy). Thus the argument from the cluster studies [10] can essentially be transferred to the periodic systems. In line with this argument is not only the top site, but also the bridge site, which is more favorable in B3LYP than in PW91, relative to the other sites. This is due to the fact that there is less donation in the case of the bridge site, compared to the threefold hollow sites, but more back donation when compared to the top site.

Another interesting property to look at is the Mulliken population, displayed in Table 5, which can be interpreted as the orbital projected densities of states, integrated up to the Fermi level (although the calculation is in fact done in a different, much easier way).

Concerning the total charges, the main difference is that the carbon charge is reduced for the bridge site (mainly less of $s + p_z$ population), and even more for the top site (like bridge less $s + p_z$,

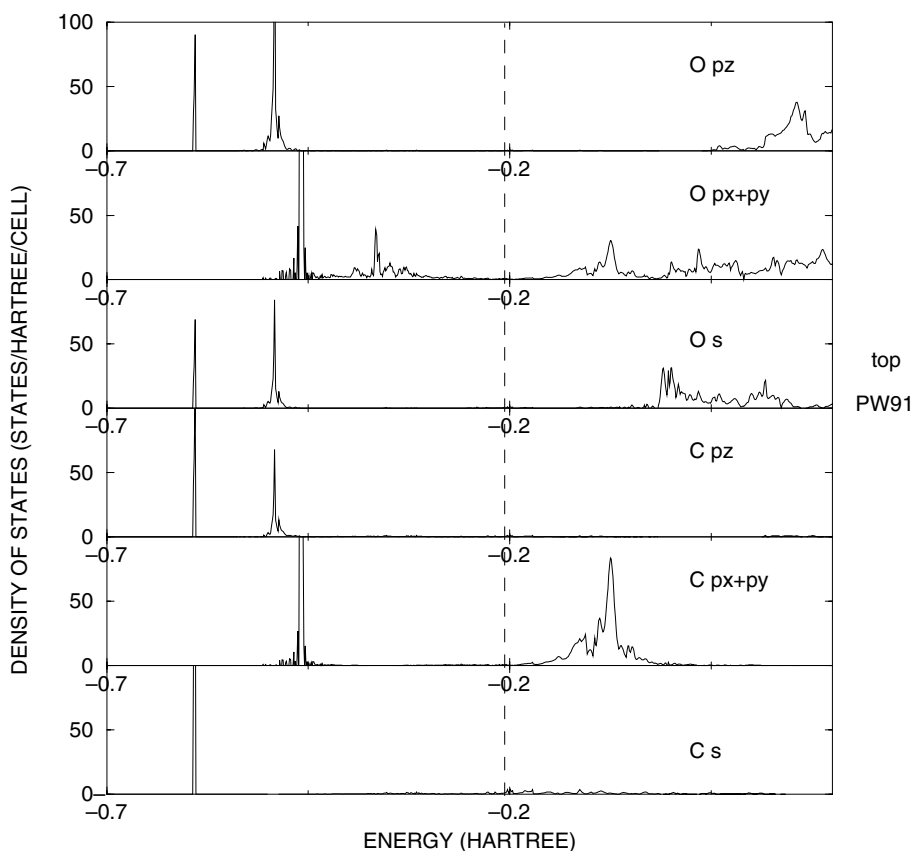


Fig. 4. Density of states, on various orbitals projected, for the top site, and the PW91 functional. The Fermi energy is indicated with a dashed line.

and in addition less $p_x + p_y$ population). As a whole, the threefold coordinated sites (fcc and hcp) have a higher charge on CO (~ 0.3 – 0.4 $|e|$), the bridge site slightly less (~ 0.2 $|e|$), and the top site has the lowest charge (~ 0.04 – 0.05 $|e|$).

The total charge on the CO molecule is slightly larger (by about 0.02 $|e|$) in PW91, compared to B3LYP. This is mainly due to the sum of the charges in the p_x and p_y orbitals which are for all sites smaller in B3LYP than in PW91. For the top site, in addition the charge in the s and p_z orbitals is larger in B3LYP than in PW91. This is consistent with the reason mentioned above: it is easier to put charge in the $2\pi^*$ orbital of the CO molecule in the case of the PW91 functional where the peaks of the unoccupied states are closer to the

Fermi energy. Also, the peaks of the occupied states are slightly more stabilized in B3LYP than in PW91. In the Blyholder model this means that donation from the 5σ orbital is energetically more favorable with the PW91 functional, and also back donation to the $2\pi^*$ orbital is more favorable with PW91. The populations are in good agreement with the numbers obtained with a Pt_{18} –CO cluster model [10].

The process of donation and back donation becomes also evident when the orbital charges of the adsorbed CO are compared with the corresponding charges of the free CO: the charge in s and p_z orbitals is reduced, and the charge of p_x and p_y orbitals increases, consistent with the Blyholder model.

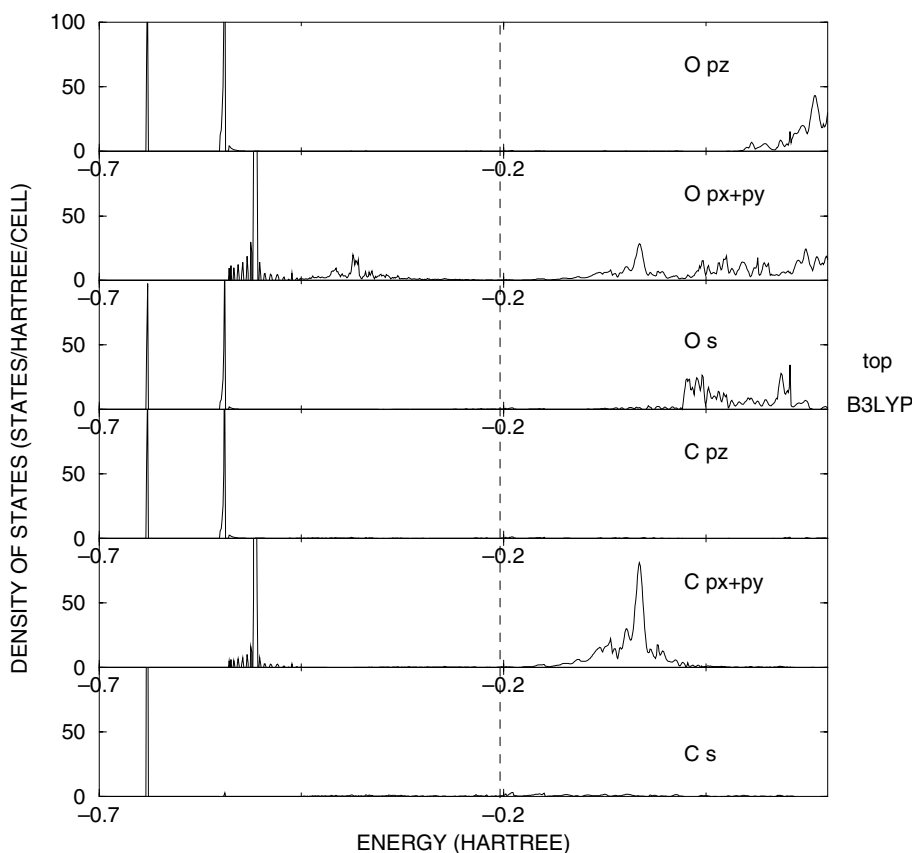


Fig. 5. Density of states, on various orbitals projected, for the top site, and the B3LYP functional. The Fermi energy is indicated with a dashed line.

We can compare the computed binding energy with the experimental results: at zero coverage, the initial adsorption energy was measured to be in the range from 1.04 to 1.78 eV (0.038 to $0.065 E_h$), and a decrease of the adsorption energy of the order of 0.1–0.2 eV (0.0037 – $0.0074 E_h$) was obtained for a coverage of one third (Ref. [24] and references therein). This is in good agreement with the data computed here, which is in the range of $0.0531 E_h$ (top, B3LYP) to $0.0639 E_h$ (fcc, PW91). The energy barrier between top and bridge site was experimentally measured to be in the range of 0.041 ± 0.007 eV ($0.0015 \pm 0.0003 E_h$) [24] which is in reasonable agreement with the order of magnitude found with the B3LYP functional in this work: the splitting between top and

bridge site is $0.0025 E_h$ in B3LYP, but $0.0013 E_h$ with the opposite sign in PW91.

There seems to be no experimental data for the geometry of the $(\sqrt{3} \times \sqrt{3})$ structure available. However, there is data from the $c(4 \times 2)$ structure where also top and bridge site are occupied [25]. The measured bond lengths are 1.85 ± 0.01 Å for the top site and 2.08 ± 0.07 Å for the bridge site. The carbon–oxygen bond length was determined to be 1.15 ± 0.05 Å. These results are in good agreement with the results computed here where the C–Pt bond length is 1.87 Å (PW91) or 1.86 Å (B3LYP) for the top site, and 2.06 Å (PW91) or 2.05 Å (B3LYP) for the bridge site; and the computed C–O bond length is also in agreement: 1.16 (PW91) or 1.15 Å (B3LYP) for the top site,

Table 5
Orbital-projected charge of CO on different adsorption sites

Site	Charge, in $ e $						
	C s + p _z	C p _x + p _y	O s + p _z	O p _x + p _y	C total	O total	CO total
PW91							
hcp hollow	4.489	1.618	5.217	2.916	6.187	8.167	14.354
fcc hollow	4.503	1.624	5.218	2.914	6.207	8.165	14.372
bridge	4.374	1.590	5.229	2.914	6.041	8.178	14.219
top	4.366	1.394	5.235	2.946	5.833	8.220	14.053
B3LYP							
hcp hollow	4.490	1.568	5.210	2.946	6.141	8.191	14.332
fcc hollow	4.506	1.576	5.209	2.944	6.168	8.189	14.357
bridge	4.379	1.532	5.224	2.942	5.995	8.202	14.197
top	4.387	1.334	5.235	2.968	5.798	8.241	14.039
Free CO molecule, PW91 ($r_e = 1.15 \text{ \AA}$)							
	4.553	1.018	5.412	2.922	5.631	8.369	14.000
Free CO molecule, B3LYP ($r_e = 1.14 \text{ \AA}$)							
	4.551	0.988	5.415	2.946	5.603	8.397	14.000

Note that the charge of the *d* basis functions is essentially constant ($\sim 0.1 |e|$ for the molecule) and not displayed.

and 1.18 \AA (PW91) and 1.17 \AA (B3LYP) for the bridge site.

3. Summary

The adsorption of CO on the Pt(111) surface was studied with the gradient corrected PW91 functional, and the hybrid functional B3LYP. A scalar-relativistic pseudopotential was used for platinum in all the studies. The adsorbate system was modeled with a slab periodic in two dimensions.

The PW91 results confirm earlier findings [6]: the fcc site is preferred compared to the top site, which is in disagreement with the experiment (the computed order was fcc, hcp, bridge, top; whereas in the experiment the top site is favored, and a minority occupancy of the bridge site was observed). The B3LYP results favor the top site, and the bridge site gets also in the range of the threefold hollow sites, so that the order is top, fcc, bridge, hcp.

An explanation based on earlier cluster studies [10] is adopted, and supported with the help of the projected density of states and the Mulliken population: in the case of the fcc site, the $2\pi^*$ orbital

has a larger occupancy than in the case of the top site. When considering an isolated molecule, this orbital is higher in energy relative to the highest occupied orbital, when the B3LYP functional is used, compared to the PW91 functional. Similarly, for the periodic system, it is found that the peak in the density of states corresponding to this orbital is higher above the Fermi energy in B3LYP, and the peaks corresponding to the occupied orbitals (especially the important 5σ orbital) are lower below the Fermi energy in B3LYP than in PW91. As a whole, PW91 will thus more favor donation from the 5σ orbital and back donation to the $2\pi^*$ orbital (the Blyholder model). This mechanism is more important for the threefold hollow sites, and thus PW91 favors these sites. B3LYP, instead, does not support this mechanism so strongly which leads to the finding that the top site is most favorable and also the bridge site gets in the range of the threefold hollow sites. This argument, which was initially based on cluster calculations and an extrapolation [10], is now confirmed with periodic calculations. Although the experimental result is not fully confirmed (top and minor bridge occupation), there seems to be evidence that hybrid functionals are better able to describe the bonding of CO to the Pt(111) surface.

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