

# Adding Pieces to the CO/Pt(111) Puzzle: The Role of Dispersion

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## Abstract

The so called *CO/Pt(111) puzzle*, the experimentally proven preference of CO to adsorb on *top* site on Pt(111) surface *versus* the standard density functional theory (DFT) methods prediction for three-fold hollow sites, was alleged to be solved by properly leveling CO frontier molecular orbitals. However, the subtle energy difference between *top* and hollow sites is of the same order of the possible contribution of dispersive forces on this interaction. Here, the role of dispersion on this system is investigated by considering the PBE, PBEsol, RevPBE, RPBE, and SOGGA11 generalized gradient approximation (GGA) based exchange correlation functionals, non-separable functionals such as N12, and the TPSS and M06-L meta-GGA type functionals together to D2, D3, D3BJ and MBD dispersion corrections. Results reinforce the advice of using M06-L for a correct description of CO adsorption site preference even if including dispersion leads to a change of site and a noticeable overestimation of the adsorption energy indicating the presence of error compensations effects. The present results also highlight that dispersion contributes in bridging the preference gap between *top* and hollow sites when other functionals are used. Dispersive forces play a role in site preference for CO on Pt(111) and it is likely that a similar situation is encountered on other late transition metals. Therefore, dispersion is to be considered to reach a complete unbiased description of CO adsorption on metals. Nevertheless, including dispersion leads to adsorption energy values which overestimate the experimental value indicating limitations of the existing, widely used, density functionals.

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## Introduction

Late transition metals are key components in several industrial chemical processes with unique electronic properties exploited in homogenous<sup>1</sup> and heterogeneous catalysis.<sup>2,3</sup> To highlight one among many, a challenging application is the usage of late transition metal based catalysts for the production of renewable fuels, hydrogen being one of the outstanding energy carriers. Nowadays H<sub>2</sub> production can run on green chemistry, but scarce and so expensive catalytic materials, such as platinum, are used as an important active phase in hydrogen generation fuel cells.<sup>4</sup> However, as it is also the case of many transition metal based catalysts, Pt is easily poisoned by carbon monoxide (CO); it adsorbs intact on the Pt surface<sup>5</sup> forming a strong chemical bond with the surface.<sup>6</sup>

Earlier measurements from temperature programmed desorption (TPD) experiments reported an estimate adsorption energy of 1.43 eV<sup>7</sup> not so far from the most recent estimates from velocity selected residence time methodology yielding  $1.47 \pm 0.04$  eV at a very low coverage regime of  $< 0.03$  monolayers (ML).<sup>8</sup> Therefore, the nature and strength of CO chemisorption on Pt(111) is well established and out of debate. This is also the for the adsorption site with a clear preference for CO on *top* of Pt surface atoms.<sup>9-11</sup> These well defined properties make CO on Pt(111) especially suited to benchmark theoretical approaches and surface models. Surprisingly, density functional theory (DFT) based calculations on periodic models using different flavors— from the local density approximation (LDA) to various generalized gradient approximation (GGA) approaches— of standard exchange correlation functionals fail to predict the experimentally observed site favoring instead the three-fold *fcc* hollow site. The same result whether all electrons are considered or employing pseudopotentials to describe the effect of core electrons on the valence electron density. The resulting situation was reviewed several years ago and lead to what is now generally known as “*The CO/Pt(111) Puzzle*”.<sup>12</sup>

This puzzle, on an apparently simple system, triggered subsequent studies aimed at providing a proper explanation for the disagreement, a suitable modification of existing methods, a test for new methods and, eventually, a solution of the problem.<sup>13,14</sup> To date it is clear that the failure arises from a wrong leveling of CO highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) with respect Pt band structure;<sup>15,16</sup> the CO bonding to transition metal surfaces can be described *via* a  $\sigma$ -donation from CO 5 $\sigma$  HOMO to the metal surface, and *backbonding* from the metal to the unoccupied

CO  $2\pi^*$  LUMO as put forward by Blyholder more than 50 years ago.<sup>17</sup> The relative strength of these two synergetic interactions depends on the local topology of the adsorption site and the electronic structure of the metal. The inherent self-interaction error of all semilocal exchange-correlation (xc) potentials makes that the partially occupied  $2\pi^*$  orbital lies too low in energy, thus artificially enhancing the *backbonding* contribution which in turn is strongest on hollow sites, thus rationalizing the unphysical preference for CO adsorption at face centered cubic (*fcc*) hollow sites of Pt(111).<sup>18</sup> Indeed, the over-contribution of *backbonding* does also explain the generally too large adsorption energies with these semilocal xc potentials which can be overestimated by more than 0.4 eV.<sup>18-20</sup> Hybrid xc functionals such as PBE0,<sup>21</sup> B3LYP,<sup>22</sup> and HSE<sup>23</sup> exhibit a reduced self-interaction error and lead to a more accurate description of thermochemistry, and so are expected to counteract the exceedingly large adsorption energy and incorrect molecular orbital leveling description of GGA type functionals. With this type of functionals the problem seems to be fixed, at least for CO on Cu(111) and Rh(111), but remains open for CO on Pt(111).<sup>19</sup> The PBE0 calculations of Wang *et al.*<sup>24</sup> for a CO on Pt(111) using a  $(\sqrt{3}\times\sqrt{3})$ -R30° supercell correctly predict the preference for the *top* site yet using the PBE optimized geometry. In fact, the systematic study of Stroppa and Kresse<sup>25</sup> using GGA and hybrid functionals and covering various surfaces find preference for the *top* site using B3LYP, but *fcc* using HSE. Other authors highlighted the use of all electron relativistic calculations to cure the leveling problem.<sup>26</sup> Interestingly, the M06-L meta-GGA functional appears to predict the correct adsorption site and also reproduces rather well the experimental adsorption energy.<sup>27</sup> The authors stated that inclusion of the kinetic energy density in M06-L *ansatz* allowed for a better description of single orbital states and of electron density decays, being both important for orbital levelling and surface modelling, where electron density exponentially decays to zero. This as well allows for a more realistic treatment of large exchange interactions, which in turn permits an improved short and medium range correlation, compensated by exchange otherwise.

In principle, one could claim that the M06-L results solve the puzzle. However, the difference between adsorption sites is quite subtle, being differences of the order of a few dozens of meV.<sup>28</sup> This order of magnitude is well within the limit accuracy of DFT methods and, in addition, other subtle effects such as dispersion contribution to the adsorption energy should not be disregarded. Indeed, M06-L is known to lack a correct description of London dispersion.<sup>29</sup> As far as we know, only a single previous study considered these non-local correlation effects on the relative stability of CO on *top* and *fcc* hollow sites.<sup>30</sup> These authors

used the vdW-DFT functional of Dion *et al.*<sup>31</sup> and compared the corresponding results to those obtained with the PBE<sup>32</sup> and RevPBE<sup>33</sup> GGA-type functionals finding that dispersion contributes to stabilize the *top* site relative to the *fcc* hollow one. However, one needs to point out that a large number of van der Waals (vdW) corrections to DFT xc functionals have been proposed in the past few years and their performance on other subtle systems is far from being uniform. This is the case of graphene on Ni(111) highlighting both some significant discrepancies between results obtained from different dispersion corrected functionals and the importance of a correct treatment of this contribution when dealing with small energy differences right in the order of the hundredths of an eV.<sup>34,35</sup>

From the previous discussion it is clear that even if the CO/Pt(111) puzzle was claimed to be solved, this was well before the blooming of methods aimed at introducing dispersion terms in the xc functionals. The results of Lazić *et al.*<sup>30</sup> using the DFT-vdW functional clearly show the importance of dispersion in discriminating the preference for the two types of sites. Because of this here we fully address the effect of dispersion by considering a variety of dispersion-corrected GGA and meta-GGA xc functionals well suited for the description of bulk and surface properties of transition metal<sup>36,37</sup> revealing that vdW forces do actually contribute to bridge the gap between *fcc* hollow and *top* sites of CO adsorption on Pt(111), yet the final effect still seems to rise from the energy level separation of CO frontier orbitals.

## Computational Details

The DFT calculations have been carried out using the VASP code exploiting periodic boundary conditions.<sup>38</sup> The projector augmented wave method was used to treat interactions between core and valence electrons.<sup>39</sup> The PBE,<sup>32</sup> PBEsol,<sup>40</sup> RPBE,<sup>41</sup> RevPBE<sup>33</sup> and SOGGA11<sup>42</sup> GGA-type functionals were considered with different types of vdW corrections. Furthermore, the non-separable gradient approximation (NGA) N12 xc functional<sup>43</sup> and the TPSS<sup>44</sup> and M06-L<sup>45</sup> meta-GGA functionals have also been considered, again combined with different of the available methods aimed at introducing dispersion.<sup>34-35</sup> Among all these methods we chose Grimme D2<sup>46</sup> and D3<sup>47</sup> empirical corrections as well as the Becke-Jonson (BJ) damping on D3.<sup>48</sup> Indeed, PBE and RPBE in conjunction with D3 or D3BJ correction is a focus to our attention as has been successfully used computational levels for the treatment of complex molecular adlayers on inorganic surfaces.<sup>49-52</sup> Note by passing by that only two-body terms were considered, known to play a main role in finite systems, although three-body

terms become important for some thermochemical properties already in finite systems.<sup>47</sup> In addition, we also consider the more physically grounded many body dispersion (MBD) method of Tkatchenko and coworkers.<sup>53,54</sup> These choices are supported from recent work showing that they provide the best treatment in systems where dispersive forces do play a key role such as graphene on Ni(111), H<sub>2</sub> storage on oxide based clusters, and many others.<sup>34,35,55</sup> Combining the different xc functionals and the above commented dispersion methods results in a total of 29 methods used to explore CO on Pt(111).

In the case of D2 correction, we used the suggested C<sub>6</sub> coefficients and R<sub>0</sub> radii as originally stated for C and O atoms, which are 1.75 and 0.7 J nm<sup>6</sup> mol<sup>-1</sup> for C<sub>6</sub>, respectively,<sup>46</sup> whereas R<sub>0</sub> values are 1.452 and 1.342 Å, respectively. For Pt, we used C<sub>6</sub> and R<sub>0</sub> values of 40.62 J nm<sup>6</sup> mol<sup>-1</sup> and 1.772 Å, as suggested later.<sup>56</sup> However, whereas for PBE and other xc functionals a scaling coefficient *s*<sub>0</sub> of 0.75 was used, it was set to unity in the case of TPSS functional.<sup>46</sup> In the case of D3 correction, the functional dependent parameters *s*<sub>6</sub>, *s*<sub>r,6</sub>, and *s*<sub>8</sub> were taken from a previous benchmark,<sup>57</sup> except for N12, which were adjusted posteriorly.<sup>58</sup> In the case of BJ damping, *s*<sub>6</sub> parameter was set to unity, whereas *a*<sub>1</sub>, *a*<sub>2</sub>, and *s*<sub>8</sub> parameters were taken from benchmarked literature.<sup>48</sup> As far as the MBD method<sup>59</sup> is considered, *surf* values were used for densely packed Pt(111), in particular, C<sub>6</sub>, *s*<sub>0</sub>, and R<sub>0</sub> were 120, 14.5, and 2.80, respectively, all in a.u. We refer to original studies for a definition of these variables.

The valence electrons density was expanded in a plane-wave basis set with a 415 eV cut-off for the kinetic energy, yet test calculations for the RPBE functional using a higher cut-off of 600 eV yield the same essentially converged results. Calculations were carried non spin-polarized for the Pt(111) slab, whose reciprocal space was sampled with 6×6×1  $\Gamma$ -centered **k**-point grid on a 54 metal atoms (3×3) supercell slab modeling the (111) surface, comprising six atomic layers, nine atoms per layer. The three bottom layers of the slab were kept fixed during the optimizations, but at the geometry belonging to the previously optimized Pt bulk using the same method. However, the three upper layers were allowed to further relax during geometry optimizations, either for the bare surface, or in the course of adsorbed CO optimizations. A minimum vacuum region of 10 Å has been placed among periodically repeated slabs in order to avoid any artificial interaction among them. Selected tests with a 20 Å vacuum width affects the *E*<sub>ads</sub> values by less than 0.01 eV. Note that during slab geometry relaxations cell parameters were kept fixed. Optimizations were performed using a Gaussian smearing of 0.2 eV energy width to speed up convergence, yet final energy

where extrapolated to 0 K (no smearing). Geometry optimizations were performed until all forces acting on relaxed atoms became less than  $0.03 \text{ eV } \text{\AA}^{-1}$ .

Focusing on *top versus hollow* competition for CO adsorption, the *top* site with CO coordinated to a surface Pt atom through its C atom has been considered whereas the face-centered cubic (*fcc*) hollow site—with no Pt atom in the second atomic layer directly beneath the CO molecule—and the hexagonal close-packed (*hcp*) hollow site—with a Pt atom in the first subsurface layer directly beneath the surface CO adsorbate; see Figure 1. Given the employed supercell, the CO surface coverage is of 1/9 monolayer (ML). We define the calculated CO adsorption energies as;

$$E_{\text{ads}} = - E_{\text{CO/Pt(111)}} + (E_{\text{CO}} + E_{\text{Pt(111)}}) \quad (1)$$

where  $E_{\text{CO/Pt(111)}}$  is the total energy of the Pt(111) slab model with the adsorbed CO molecule,  $E_{\text{CO}}$  is the energy of an isolated CO molecule, and  $E_{\text{Pt(111)}}$  is the energy of the optimized clean Pt (111) surface slab model. With this definition, stable adsorption/absorption corresponds to positive  $E_{\text{ads}}$  values. The isolated CO molecule has been calculated placing it in an asymmetric box of  $9 \times 10 \times 11 \text{ \AA}$  and carrying the calculation at the  $\Gamma$  point. Note that the adsorption energy as defined in Equation (1) is directly comparable to the heat of adsorption measured in microcalorimetry experiments<sup>60</sup> although a proper comparison should include the difference in zero point energy (ZPE) of the gas phase and adsorbed molecule. The vibrational frequency of CO at *top* and *fcc* site is roughly of  $2100$  and  $1800 \text{ cm}^{-1}$ , respectively.<sup>9</sup> Hence, the effect of the ZPE in the difference of adsorption energy of CO on the Pt(111) surface is of less than  $0.02 \text{ eV}$  and favoring the *fcc* site.

## Results and Discussion

The complete set of results for adsorption energy at the *top* and hollow sites plus the corresponding relevant structural parameters is summarized in Table 1 for the total of 29 methods explored. Additionally, calculated total energy values for the optimized structures of adsorbed CO and of the isolated gas phase molecule and relaxed surface model are provided in the supporting information (SI) file for all methods used in the present work. The SI also collects computational details and optimized structures, again for each one of the density functionals explored. First, we focus on the magnitude of the calculated adsorption energy values. In order to facilitate the analysis, Figure 2 shows the  $E_{\text{ads}}$  values for CO adsorbed on *top* and *fcc* hollow sites, the figure also highlights the range of experimental values spanning the  $1.4\text{-}1.5 \text{ eV}$  interval.<sup>7,8,61</sup> From Figure 2 it is clear that solely RevPBE and RPBE,

especially designed to improve the adsorption energy of CO on metals,<sup>62</sup> but at the expenses of worsening the description of bulk transition metals,<sup>34</sup> meet the experimentally measured adsorption energy. Interestingly, results from TPSS and M06-L meta-GGA functionals closely follow the RPBE prediction. However, the agreement to experiment is less satisfactory, even for RevPBE and RPBE, when considering explicitly the contribution of dispersion to the interaction. Figure 2 clearly shows that the addition of any of the here explored vdW corrections results in clear overestimation of the experimental adsorption energy by 0.3-0.5 eV.

Apart from the total value of the adsorption energy, Figure 2 also allows one to compare the calculated values of adsorption energy for on *top* and hollow sites. For each method, the close similarity between values for *top* and hollow sites predicted from the different computational approach pinpoint the underlying factors that subtly favor on site over the others. For a better visualization of this trend Figure 3 shows the difference energy ( $E_{\text{diff}}$ ) of the  $E_{\text{ads}}$  of hollow sites and that of *top* site. With this definition, negative  $E_{\text{diff}}$  values denote a higher stability than for the *top* site and inspection of Figure 3 shows that the majority of methods fail in reproducing the experimentally observed preference for the on *top* site. There are, however, some aspects worth of being commented: On one hand, note how, in average terms, dispersion brings the stability of CO on hollow sites closer to on *top* sites. This is true for D2, D3, and MBD corrections, yet it does not hold for D3BJ, where its application worsens the description for most cases, in line with a slightly worse description of graphene/Ni(111) interactions as earlier reported.<sup>35</sup> Taking this into account, and focusing the attention to the PBE based cases, one observes how addition of D2 improves the description by 13 meV in average, whereas successive treatment by D3 and MBD further stepwise improves it by 20 and 8 meV, respectively. However, the D2 correction does not always improve the description since on other GGA, NGA, or meta-GGA functionals, such as SOGGA11, RevPBE, RPBE, N12, and TPSS, the opposite trend is observed. Indeed, SOGGA11 shows relatively large  $E_{\text{ads}}$  values, in line with previous studies highlighting its overbinding.<sup>58</sup> Interestingly, the in principle more accurate D3 parameterization of dispersion leads to a proper decrease of  $E_{\text{diff}}$ . In the case of RevPBE and RPBE, the description compared to pure PBE is improved by 44 and 17 meV, respectively, and it goes to 25 meV in the case of TPSS. Notice as well the great improvement when applying the D3 correction to N12 functional, approaching the accuracy of RevPBE-D3 and RPBE-D3. Hence, present results show that relative stability of hollow and *top* sites for the CO adsorption on Pt(111)

surface tends to decrease when dispersion is taken into account, in accordance to previous findings.<sup>30</sup>

An issue worth to tackle separately is that of the local M06-L functional, which has already been reported as correctly describing the preference of *top* versus hollow site.<sup>27</sup> The present results further confirm this prediction, although the alleged preference for *top* over *fcc* hollow by 360 meV could not be reproduced despite using same computing package and carrying out the study at a similar low coverage. The only difference is in the energy cutoff of 415 eV in the present work, and 500 eV in the previous<sup>27</sup> but also the use of slightly different surface slab model, both containing 6 atomic layers but relaxed 3+3 in the present work and symmetrically the top and bottom two layers with the two innermost fixed in Ref. 27. The disagreement however is highly reduced when comparing PBE and RevPBE results, where the earlier work in Ref. 27 reports an *fcc* hollow preference by 100 and 90 meV, respectively, thus much closer to present values of 169 and 49 meV, respectively with the differences in the range of numerical accuracy. Regardless of this small discrepancy, M06-L is the unique explored xc capable of favoring *top* over *fcc* site. Note however that addition of vdW, on the contrary, slightly favors *fcc* hollow by 13 and 64 meV at D2 and D3 levels. Therefore, as far as the contribution of dispersion is concerned, only Grimme D3 correction on RPBE is capable to equal preference of *top* to *fcc* hollow site, but with a too large value of the adsorption energy.

The trends in interatomic distances provide additional information regarding the performance of the 20 computational methods explored. Figure 4 shows the CO molecule interatomic distance when adsorbed over *top* site, or over the *fcc* or hcp hollow sites, together with the experimentally derived distance from low energy electron diffraction (LEED) experiments by Ogletree *et al.*,<sup>6</sup> reporting a  $d(\text{C-O})$  distance of  $1.15 \pm 0.05$  Å. One can observe that CO bond length does not allow differentiating among sites. However, the situation is different when considering  $d(\text{C-Pt})$ , also shown in Figure 4 compared to those of  $1.85 \pm 0.10$  Å also obtained from LEED. Results clearly highlight how only *top* site meets the structural experimentally determined data, and none of the hollow sites, whatever the computational method employed, meets this requirement. *Top* site is definitely the preferred to CO, however, no significant distinction among the situations described employing various DFT xc functionals and vdW corrections is found.

Notice that, because of the problems in convergence for metallic systems and the exceedingly high computational cost when a plane wave basis set is used, hybrid functionals



were not explicitly considered in the present study. However, as above-explained, they tend to correctly level the  $2\pi^*$  CO orbital, and, consequently, hybrid functionals tend to describe the preference of *top* versus hollow sites.<sup>24,25</sup> However, the poorer description of the delocalized band structure of metals seems to be the main reason why hybrid functionals excessively overestimate CO adsorption energies. Assuming that the vdW contribution to  $E_{\text{ads}}$  computed for GGA can be added to the results from hybrid xc functionals, this overestimation will be further increased by  $\sim 0.3$  eV, although it is likely that vdW effects would help in the preference of adsorption on *top* versus hollow by  $\sim 0.05$  eV.

## Conclusions

In this work we investigated the role of dispersion contribution in the interaction of CO on Pt(111) with the aim to discern whether these play a key role in the preference of CO for atop sites of the Pt(111) surface. To this end, up to 29 different density functionals including or not dispersions have been considered. From the complete set of results, it appears that only M06-L is able to reproduce the correct CO adsorption site although only when dispersion terms are not included which indicates some error compensation effects. This claim is supported by the results of M06-L when dispersion is included which noticeably overestimate the adsorption energy. In general, inclusion of dispersion assists in bridging the gap in between *top* and hollow sites, and its effect is in the order of the site difference in energy for CO on Pt(111), as well as on other late transition metals, and so, yet not fully determining, it is a factor to be considered in order to get a complete unbiased description of CO adsorption, in particular, yet to other simple molecules in general.

Nevertheless, inclusion of dispersion leads to a consistent overestimation of the adsorption energy indicating that, in spite of an overall and confirmed success of DFT based methods on describing the interactions and energetic of reactions at surfaces,<sup>63</sup> the accuracy of existing density functionals needs to be improved. The present results also warn on the *ad hoc* modification of functionals to reproduce adsorption energies while neglecting physically meaningful contributions as dispersion.

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## Supporting information

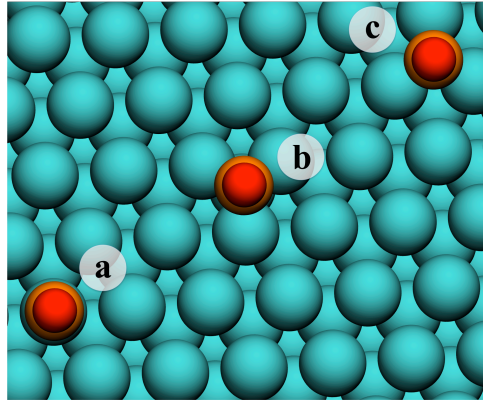
The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxxxxxxxxxxxxx

Table S1. Total energy of CO, relaxed slab model of Pt(111) and of the optimized structure of CO adsorbed at the surface model as predicted by the different functionals used in the present work. All values are in eV.

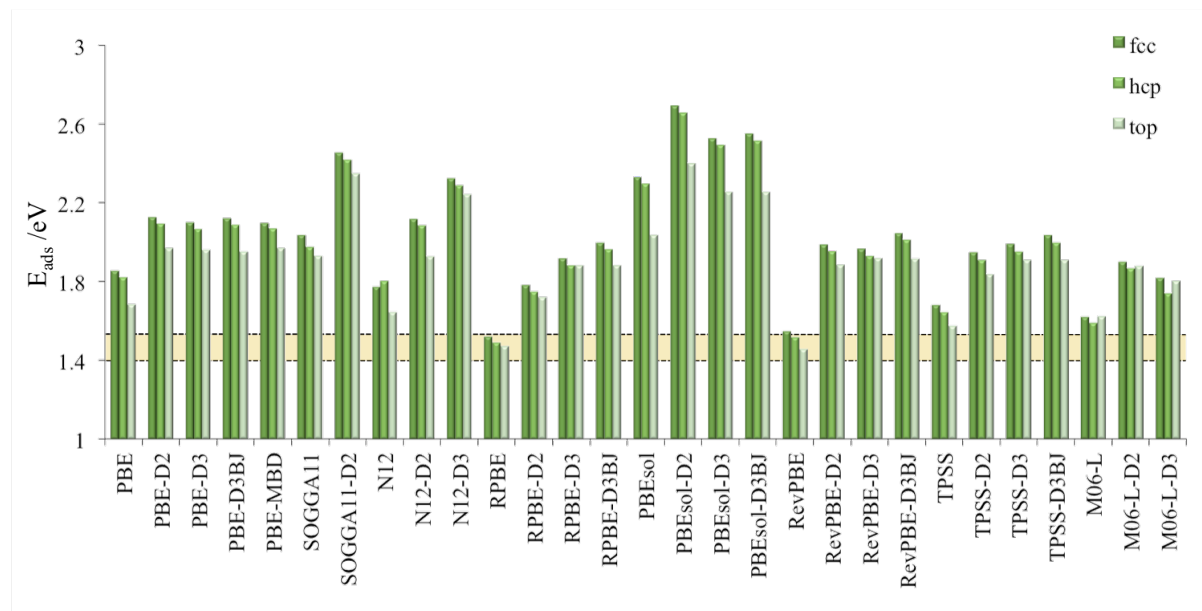
Computational details (INCAR files): Default parameters and Functional settings

Structural information: Optimized geomtr for each fuctional (CONTCAR files)

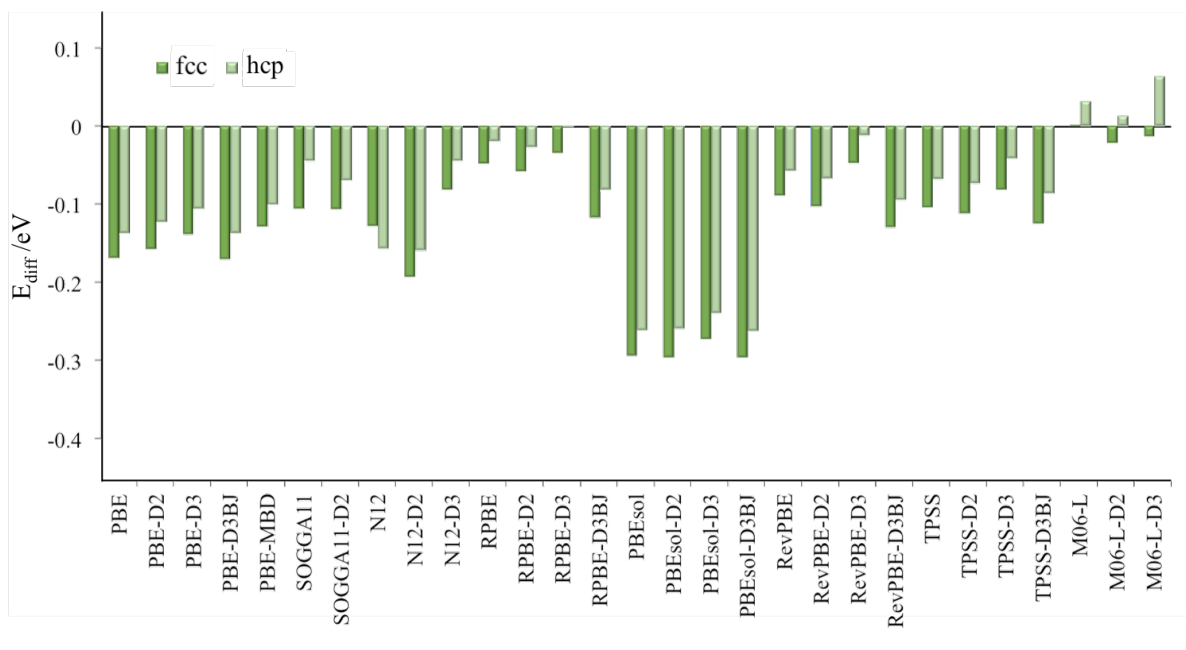
**Figure 1.** Top view of CO adsorption sites on Pt(111) surface, including a) *top*, b) *hcp* and c) *fcc* hollow sites. Pt, C, and O atoms positions are denoted by cyan, orange, and red spheres, respectively.



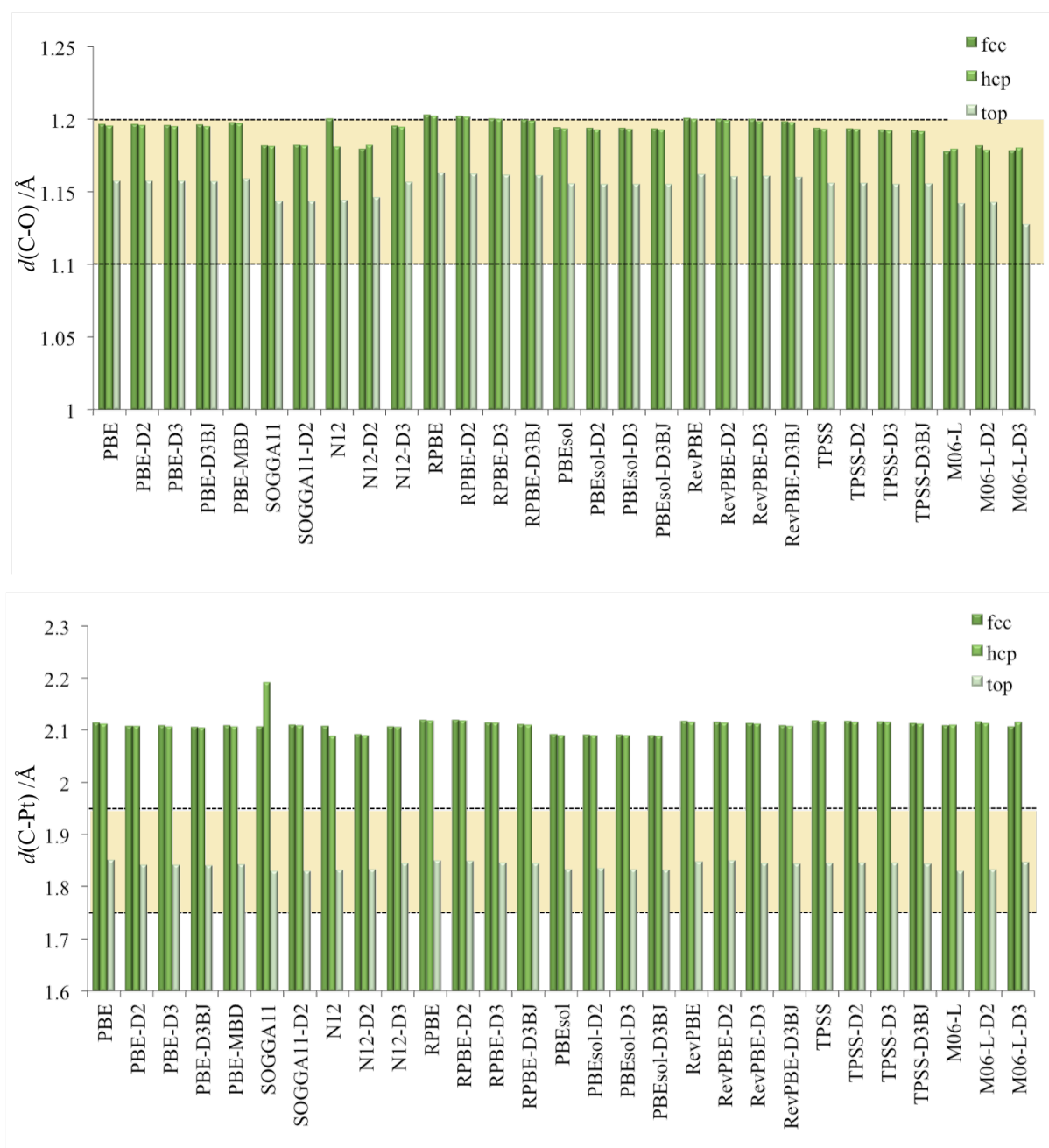
**Figure 2.** Adsorption ( $E_{\text{ads}}$ ) energies, for CO adsorbed on *fcc*, *hcp*, or *top* sites on Pt(111) surfaces as obtained employing various DFT xc functionals, including or not a treatment of dispersive force. Experimental range of values is delimited by a yellowish region.



**Figure 3.** Difference in adsorption energies ( $E_{\text{diff}}$ ) in between hollow and top site for CO adsorption on Pt(111) surface, as obtained employing various DFT xc functionals, including or not a treatment of dispersive forces.



**Figure 4.** Interatomic CO molecule distance,  $d(\text{C-O})$  (top panel), when CO adsorbed on top site of a Pt surface atom of Pt(111), or over *fcc* or *hcp* hollow sites, as well the distance among C atom and those surface Pt atoms involved in its adsorption,  $d(\text{C-Pt})$  (bottom panel), as obtained employing various DFT xc functionals, including or not a treatment of dispersive forces. Experimental range of values is delimited by a yellowish region.



**Table 1.** Adsorption energy ( $E_{\text{ads}}$  in eV) and relevant distances in Å for CO adsorbed on *top*, *fcc* or *hcp* hollow sites of the surface Pt(111) as predicted from difference xc functionals, including or not a treatment of dispersive forces.

<b>Method</b>	<b>Site</b>	$E_{\text{ads}}$	$d_{\text{C-O}}$	$d_{\text{C-Pt}}$
<b>PBE</b>	<i>fcc</i>	1.854	1.196	2.114
	<i>hcp</i>	1.822	1.195	2.112
	<i>top</i>	1.685	1.157	1.851
<b>PBE-D2</b>	<i>fcc</i>	2.128	1.197	2.108
	<i>hcp</i>	2.093	1.196	2.107
	<i>top</i>	1.970	1.158	1.842
<b>PBE-D3</b>	<i>fcc</i>	2.099	1.196	2.108
	<i>hcp</i>	2.066	1.195	2.107
	<i>top</i>	1.960	1.158	1.841
<b>PBE-D3BJ</b>	<i>fcc</i>	2.121	1.196	2.106
	<i>hcp</i>	2.088	1.195	2.105
	<i>top</i>	1.951	1.157	1.841
<b>PBE-MBD</b>	<i>fcc</i>	2.097	1.198	2.109
	<i>hcp</i>	2.068	1.197	2.107
	<i>top</i>	1.968	1.159	1.842
<b>SOGGA11</b>	<i>fcc</i>	2.036	1.182	2.107
	<i>hcp</i>	1.974	1.181	2.192
	<i>top</i>	1.930	1.143	1.830
<b>SOGGA11-D2</b>	<i>fcc</i>	2.454	1.182	2.110
	<i>hcp</i>	2.417	1.182	2.109
	<i>top</i>	2.348	1.144	1.830
<b>N12</b>	<i>fcc</i>	1.773	1.200	2.108

	<i>hcp</i>	1.802	1.181	2.088
	<i>top</i>	1.645	1.144	1.832
<b>N12-D2</b>	<i>fcc</i>	2.119	1.180	2.092
	<i>hcp</i>	2.085	1.182	2.089
	<i>top</i>	1.926	1.146	1.833
<b>N12-D3</b>	<i>fcc</i>	2.325	1.195	2.106
	<i>hcp</i>	2.288	1.195	2.106
	<i>top</i>	2.243	1.157	1.845
<b>RPBE</b>	<i>fcc</i>	1.521	1.203	2.120
	<i>hcp</i>	1.492	1.202	2.118
	<i>top</i>	1.472	1.163	1.850
<b>RPBE-D2</b>	<i>fcc</i>	1.781	1.202	2.120
	<i>hcp</i>	1.749	1.202	2.118
	<i>top</i>	1.722	1.162	1.850
<b>RPBE-D3</b>	<i>fcc</i>	1.918	1.200	2.114
	<i>hcp</i>	1.883	1.200	2.114
	<i>top</i>	1.883	1.162	1.846
<b>RPBE-D3BJ</b>	<i>fcc</i>	1.997	1.200	2.111
	<i>hcp</i>	1.962	1.199	2.110
	<i>top</i>	1.880	1.161	1.845
<b>PBEsol</b>	<i>fcc</i>	2.330	1.194	2.091
	<i>hcp</i>	2.297	1.193	2.090
	<i>top</i>	2.036	1.156	1.833
<b>PBEsol-D2</b>	<i>fcc</i>	2.694	1.194	2.090



	<i>hcp</i>	2.657	1.193	2.089
	<i>top</i>	2.398	1.155	1.835
<b>PBEsol-D3</b>	<i>fcc</i>	2.526	1.194	2.091
	<i>hcp</i>	2.493	1.193	2.090
	<i>top</i>	2.254	1.155	1.833
<b>PBEsol-D3BJ</b>	<i>fcc</i>	2.550	1.194	2.090
	<i>hcp</i>	2.515	1.193	2.088
	<i>top</i>	2.253	1.155	1.833
<b>RevPBE</b>	<i>fcc</i>	1.548	1.201	2.117
	<i>hcp</i>	1.517	1.200	2.116
	<i>top</i>	1.459	1.162	1.849
<b>RevPBE-D2</b>	<i>fcc</i>	1.989	1.200	2.115
	<i>hcp</i>	1.953	1.199	2.114
	<i>top</i>	1.886	1.161	1.850
<b>RevPBE-D3</b>	<i>fcc</i>	1.965	1.200	2.113
	<i>hcp</i>	1.930	1.199	2.112
	<i>top</i>	1.918	1.161	1.844
<b>RevPBE-D3BJ</b>	<i>fcc</i>	2.046	1.200	2.109
	<i>hcp</i>	2.011	1.198	2.108
	<i>top</i>	1.916	1.160	1.844
<b>TPSS</b>	<i>fcc</i>	1.681	1.194	2.119
	<i>hcp</i>	1.645	1.193	2.117

	<i>top</i>	1.576	1.156	1.844
<b>TPSS-D2</b>	<i>fcc</i>	1.949	1.193	2.117
	<i>hcp</i>	1.910	1.193	2.115
	<i>top</i>	1.837	1.156	1.846
<b>TPSS-D3</b>	<i>fcc</i>	1.990	1.193	2.117
	<i>hcp</i>	1.951	1.192	2.115
	<i>top</i>	1.909	1.155	1.846
<b>TPSS-D3BJ</b>	<i>fcc</i>	2.035	1.192	2.113
	<i>hcp</i>	1.996	1.192	2.112
	<i>top</i>	1.910	1.156	1.844
<b>M06-L</b>	<i>fcc</i>	1.622	1.178	2.108
	<i>hcp</i>	1.592	1.180	2.110
	<i>top</i>	1.624	1.142	1.830
<b>M06-L-D2</b>	<i>fcc</i>	1.900	1.182	2.116
	<i>hcp</i>	1.865	1.179	2.114
	<i>top</i>	1.878	1.143	1.833
<b>M06-L-D3</b>	<i>fcc</i>	1.818	1.178	2.107
	<i>hcp</i>	1.740	1.180	2.115
	<i>top</i>	1.804	1.127	1.847

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## Graphic for TOC

