CO on Pt(111) puzzle; A possible solution

Ilya Grinberg, Yashar Yourdshahyan, and Andrew M. Rappe

Department of Chemistry and Laboratory for Research on the Structure of Matter University of Pennsylvania, Philadelphia, PA 19104–6323

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Abstract

CO adsorption on the Pt(111) surface is studied using first-principles methods. As found in a recent study [Feibelman *et al.*, J. Phys. Chem. B **105**, 4018 (2001)], we find the preferred adsorption site within density functional theory to be the hollow site, whereas experimentally it is found that the top site is preferred. The influence of pseudopotential and exchangecorrelation functional error on the CO binding energy and site preference was carefully investigated. We also compare the site preference energy of CO on Pt(111) with the reaction energy of formaldehyde formation from H₂ and CO. We show that the discrepancies between the experimental and theoretical results are due to the generalized gradient approximation (GGA) treating different bond orders with varying accuracy. As a result, GGA results will contain significant error whenever bonds of different bond order are broken and formed.

I. INTRODUCTION

The interactions of small molecules on metal surfaces play an important role in many industrial processes, such as automotive catalysis, corrosion, tribology, and gas sensing. These processes have been the subject of intensive experimental and theoretical investigation¹. Due to its simplicity, carbon monoxide frequently serves as a probe molecule in studies aiming to understand the nature of molecule-metal interactions. The insights gained from CO/metal surface studies can then be transferred to more complex systems. A particularly well-studied system is CO on the Pt(111) surface. The adsorption of CO on Pt(111) has been studied experimentally at various coverages and pressures.^{2,3} Scanning tunneling microscopy (STM), low energy electron diffraction (LEED), and infrared adsorption (IR) experiments have shown that in ultra-high vacuum conditions CO adsorbs on top sites exclusively at low coverages and forms a $c(4 \times 2)$ top-bridge overlayer at half-monolayer coverage⁴⁻¹⁴. Yeo *et al.* measured the CO chemisorption energy calorimetrically, finding that it decreases from about 1.9 eV at low coverages to 1.2 eV at half-monolayer coverage¹⁵.

Several phenomenological models of CO-metal surface bonding have been proposed. The most widely used conceptual framework for small molecule adsorption on surfaces is the Blyholder model¹⁶, with electron donation from the CO 5σ orbital to the metal and back donation from the metal to the CO $2\pi^*$, coupling the CO levels to the metal *sp* states and *d* states. Building on the Blyholder model, Hammer *et al.* have proposed a quantitative model for CO chemisorption energy in terms of the energy of the center of the metal *d* bands¹⁷. Their model gives reasonably good agreement with experiment. However, the Blyholder model has been recently challenged by Fohlisch *et al.*, who have studied CO adsorbed on the top, bridge and hollow sites on Ni(100) with X-ray emission spectroscopy and *ab initio* calculations¹⁸. They conclude that chemisorption energy is the result of a balance between the repulsive σ and attractive π interactions, leading to very different electronic structures for different adsorption sites, despite similar binding energies.

Density functional theory^{19,20} (DFT) calculations have also been carried out to study this system at both the local density approximation $(LDA)^{21,22}$ and generalized gradient approximation $(GGA)^{23,24}$ levels. Jennison *et al.* studied CO adsorption on a 91-atom Pt cluster simulating a (111) surface²⁵. They found the top site to be preferred, followed by bridge, with hcp less stable. Philipsen *et al.* found a 0.24 eV difference between the binding energies of the top and hcp sites, with the top preferred when relativistic effects were included in the calculation²⁶. Even though their study was done using periodic boundary conditions, they only used two metal layers to represent the platinum surface in their calculations. Lynch and Hu carried out a GGA study of the adsorption of CO on various Pt(111) surface sites²⁷. In this study, the bottom two layers of Pt were frozen at bulk positions, but the top layer was allowed to relax. Using the same four-site, three-layer approximation they obtained chemisorption energies for CO on fcc, hcp, top and bridge sites at quarter monolayer coverage. They obtained a top site binding energy of 1.89 eV, with bridge E_{chem} of 2.00 eV, hcp of 2.00 eV and 2.09 eV for the fcc site. The preference of hollow sites over the top site as well as the values of the binding energies are not in agreement with experiment.

In a recent study, Feibelman *et al.* showed²⁸ that the results of Jennison *et al.* and Lynch et al. as well as other earlier calculations suffered from several convergence problems. When approximations such as basis set size, k-point sampling and slab thickness were converged, DFT calculations on the CO/Pt(111) system using a variety of functionals in pseudopotential (PSP), projector-augmented wave (PAW) and full-potential linearized augmented plane wave (FLAPW) approaches consistently preferred the hollow site over the top site. Their results are summarized in Tables I and II. While the hollow site was always preferred, the magnitude of the energy difference varied depending on the core electron approximation and exchange-correlation functional used. LDA calculations give about 0.4 eV for the site preference energy (E_{t-h}) , while GGA results vary from 0.25 eV obtained with PW91/PBE ultra-soft potential calculations, to 0.13 eV obtained with PW91/PAW to 0.10 eV obtained with FLAPW calculations. Feibelman *et al.* also report calculations for CO/Cu(111) and CO/Rh(111), where GGA calculations again prefer the fcc site, while experimentally the top site is preferred. GGA and experiment do agree in the case of Ru(0001), where GGA predicts the experimentally-observed adsorption on the top site. In the case of CO/Pd(111), GGA predicts the experimentally-observed fcc site adsorption. They conclude that GGA/LDA tends to favor higher coordination, which is correct in the case of Pd(111) but incorrect for surfaces where the top site is preferred. However, the reasons for discrepancies between LDA

	$\Theta(ML)$	method	XC	E_{t-h}
$3 \times 2\sqrt{3}$	1/12	VASP,USP	PW91	0.25
2×2	1/4	DACAPO,USP	PW91	0.23
2×2	1/4	DACAPO,USP	PBE	0.24
2×2	1/4	DACAPO,USP	RPBE	0.16
2×2	1/4	DACAPO,USP	LDA	0.45
$c(4 \times 2)$	1/4	VASP,USP	LDA	0.41
$c(4 \times 2)$	1/4	DACAPO,USP	PW91	0.23
$c(4 \times 2)$	1/4	VASP,USP	PW91	0.18
$c(4 \times 2)$	1/4	VASP,PAW	PW91	0.13
$\sqrt{3} \times \sqrt{3}$	1/3	DACAPO,USP	PW91	0.23
$\sqrt{3} \times \sqrt{3}$	1/3	WIEN,FLAPW	PW91	0.10

TABLE I. Results of DFT calculations of Feibelman *et al.*²⁸ for site preference energy for various coverages and methods. ΔE_{t-h} is the CO/Pt(111) difference between top and hcp site chemisorption energies. All energies are in eV.

and GGA results and between PSP, PAW, and FLAPW calculations are not resolved, nor do they propose a way to estimate the site preference error. The PSP-GGA DFT method has proven to be reliable and accurate for a wide variety of solid-state systems, so the inability of GGA calculations to predict site preference of CO on metal surfaces is puzzling.

The results from the pioneering work of Feibelman *et al.* raise several questions. First, what is the reason for the discrepancies between PSP and all-electron results, and can a closer agreement between PSP and all-electron calculations be obtained? Second, are the site preference errors limited to CO on (111) surfaces, or are similar effects found with other molecules and/or other surfaces? Third, does the error in E_{t-h} come from an error in E_{chem} of a particular site, or a combination of errors in E_{chem} of both sites? The answers to all of these questions will help identify the reason for DFT failure for CO/Pt(111).

In PSP-DFT calculations there are only two uncontrolled approximations: the replace-

fcc sites, from calculations of Feibelman *et al.* ²⁸ Experimental results for the top and the bridge sites are taken from Ref. 5 and Ref. 6, and for the hollow site from Ref. 28 $\frac{\omega_{C-O} \text{ Exp.}}{\omega_{C-O} \text{ DFT}} \frac{\omega_{C-Pt} \text{ Exp.}}{\omega_{C-Pt} \text{ DFT}}$ top 2095 2140 466 461

370

1926

1832

393

342

bridge

 \mathbf{fcc}

1845

1750

TABLE II. Calculated normal mode frequencies (cm^{-1}) for CO on Pt(111) at top, bridge and

ment of the nucleus and the core electrons with a pseudopotential, and the form of the
exchange-correlation functional. The effect of pseudopotential error on adsorption energies
has not been examined but has been assumed to be small. Exchange-correlation functional
error has been known to affect binding energies, most notably for LDA. Hammer $et al$. stud-
ied the effect of different exchange-correlation functionals on the binding energy of CO on
the fcc site of the $Pd(111)$ surface ²⁴ . They found that LDA overbinds by about 1.0 eV, while
PBE GGA overbinds by 0.2–0.3 eV and RPBE and revPBE GGA overbind by 0.1–0.2 eV.
The source of the GGA and LDA DFT site preference errors must lie in either one or both
of the uncontrolled approximations. For FLAPW calculations there is no pseudopotential
error, so the wrong site preference must come entirely from the functional error. For PSP
calculations, both PSP and XC functional errors can contribute to error in chemisorption
energy, with the PSP and XC effects either cooperating or canceling out. In the next section,
we examine PSP error.

II. PSEUDOPOTENTIAL EFFECTS

Pseudopotential error can affect different bonds in the CO/Pt(111) system differently. In addition to freezing the core states, the pseudopotential approach involves changing the nuclear potential inside a core radius r_c . If the wave function of one atom interacts with the potential inside the core region of another atom, the unphysical nature of the pseudopotential will be manifested in the results. The CO bond will be affected by overlap of core radii for typical carbon and oxygen pseudopotentials, due to the very short CO bond length (1.12– 1.19 Å). However, the C–Pt and Pt–Pt bonds will not have core overlap, since these bonds are longer, 1.85–2.1 Åand 2.77 Årespectively. Thus, core overlap in the CO bond introduces an additional, albeit controlled error into PSP-DFT calculations which can either cooperate or cancel out with the XC functional error. Calculations by Feibelman *et al.* suggest that for E_{t-h} DFT error is dominant, while PSP error affects E_{t-h} by 0.15 eV at most.

To investigate the effects of PSP core overlap, we carry out a series of calculations on the CO/Pt(111) system. We use several carbon and oxygen pseudopotentials, gradually eliminating core overlap from the CO bond, while keeping the same Pt pseudopotential for all calculations. This allows us to obtain the accuracy limit of DFT calculations using the pseudopotential approach.

We carry out DFT calculations on the CO/Pt(111) system at quarter coverage using optimized norm-conserving pseudopotentials³⁰ and the PBE GGA functional²³. The platinum pseudopotential was created using a wave function averaging relativistic construction³¹, with the designed non-local method³² used to achieve good norm and eigenvalue transferability³³. We use an 81 Ry plane-wave cutoff for PSP 1 through PSP 5. The unusually high planewave cutoff allows us to use carbon and oxygen pseudopotentials without core overlap in CO. All carbon and oxygen pseudopotentials were created from the same reference configuration, differing in their core radii; PSP 6 and PSP 7 were created at 50 Ry cutoff. We use five metal layers with six layers of vacuum to model the Pt(111) surface, keeping the three bottom layers fixed and relaxing the coordinates of the top two layers. All calculations are done in a $c(4 \times 2)$ unit cell using a $4 \times 4 \times 1$ grid of Monkhorst-Pack k-points³⁴ to sample the reducible Brillouin zone. For every set of carbon and oxygen PSPs, we calculate the binding energy at the top and hollow sites. The differences E_{t-h} are shown in Figure 1; additional properties are listed in Table III. The positive values of E_{t-h} mean that the hcp site is lower in energy than the top site.

As can be seen from Figure 1, the hcp site is always preferred by 0.01–0.09 eV, in

TABLE III. Results of DFT-GGA calculations for the CO/Pt(111) system for various carbon and oxygen pseudopotentials. PSPs 1-5 were created with 81 Ry plane-wave cutoff, and PSPs 6 and 7 were created with 50 Ry plane-wave cutoff. Shown are the CO chemisorption energy (E_{chem}), CO bond length (R_{CO}), and the site preference energy $E_{\text{t-h}}$. The values for the hollow site are shown in parentheses. Energies are in eV, core radii are in a_0 , and bond lengths are in Å.

	$r_c^{\mathrm{O}}, r_c^{\mathrm{C}}$	$E_{\rm chem}$	$R_{ m CO}$	E_{t-h}
	(a_0)	(eV)	(Å)	(eV)
PSP 1	0.50, 0.58	1.73(1.81)	1.165(1.202)	0.082
PSP 2	0.58, 0.64	1.73(1.81)	1.164(1.201)	0.079
PSP 3	0.64,0.69	1.73(1.80)	1.163(1.200)	0.074
PSP 4	0.69, 0.74	1.73(1.80)	$1.161 \ (1.196)$	0.068
PSP 5	0.74, 0.79	1.73(1.78)	1.154(1.194)	0.055
PSP 6	0.74, 0.79	1.72(1.75)	1.148 (1.181)	0.030
PSP 7	0.79, 0.85	1.72(1.73)	$1.146 \ (1.172)$	0.007
AE				0.100^{28}
Exp		1.68 ± 0.12^{15}		

disagreement with experiment but in agreement with calculations by Feibelman *et al.* As expected, the effect of core overlap is exponential in r_c . This implies that past a threshold of 1.25–1.35 a_0 ($r_c^O + r_c^C$) a small change in r_c will produce a significant error in calculated DFT properties. It is gratifying to note that E_{t-h} converges as we eliminate core overlap and that the E_{t-h} obtained by us using the best carbon and oxygen pseudopotentials is essentially identical with that by Feibelman *et al.* using FLAPW calculations. We have also used different Pt PSPs with the same C and O PSPs, but found only a small (about 0.02 eV) variation of E_{t-h} with Pt PSP. Our results suggest that PSP calculations with no core overlap preserve almost all of the accuracy of an all-electron approach, with a PSP error of less than 0.02 eV. However, using pseudopotentials unconverged with respect to core overlap can lead to significantly larger PSP error (0.1 eV or more) in E_{t-h} as well as in other properties.

III. GENERALITY OF SITE PREFERENCE ERROR

A second question raised by the results of Feibelman *et al.* is the generality of site preference errors. It is obviously important to know if the failure of DFT/GGA is confined to CO on (111) metal surfaces, or if this effect is found in other types of systems. We first examine the results in the literature for CO on (100) metal surfaces. Eichler and Hafner found in PSP-GGA calculations of CO adsorption on $Rh(100)^{35}$ that at quarter monolayer coverage the bridge and the hollow sites were preferred over the top site, while experiment showed the top and bridge site to be occupied at low coverages with no hollow site occupation. The site preference energies from their calculations overestimate the energetic preference for bridge and hollow site adsorption and underestimate the height of the barrier for the migration from the top site to the bridge site.

For Cu(100) experimentally only top site adsorption is seen. Recently Favot *et al.* examined the adsorption of CO on Cu(100) using LDA and GGA³⁶. The site preference energies from their calculations are summarized in Table IV. They find E_{t-h} of 0.18 eV for LDA and E_{t-h} of -0.09 eV for GGA approximations, showing the same trend of a reduction in E_{t-h} on going from LDA to GGA as the results of Feibelman *et al.* It therefore seems very likely that the explanation for the discrepancies between top-hollow site preference in CO/(100) metal surface systems and the top-hollow site preference in CO/(111) systems are of the same origin.

To explore the generality of this error, it is instructive to see how DFT performs for a gas phase system which exhibits a similar bond breaking/formation pattern. We therefore examine the energy of formaldehyde formation (ΔE_{form}) from CO and H₂ (H₂+CO \rightarrow H₂CO). To remove the pseudopotential error, we gradually reduce the core radii of the carbon and oxygen pseudopotentials to eliminate core overlap, while keeping the same hydrogen PSP.

	$E_{\rm chem}^{ m top}$	$E_{\rm chem}^{ m bridge}$	$E_{\rm chem}^{\rm hollow}$	$E_{\rm t-h}$
	(eV)	(eV)	(eV)	(eV)
CO/Cu(100) LDA ³⁶	1.1	1.15	1.28	0.18
$CO/Cu(100) PBE^{36}$	0.78	0.75	0.69	-0.09
$CO/Rh(100)$ PW91 35	2.0	2.15	2.2	0.20

TABLE IV. Results of DFT calculations for CO adsorption on (100) metal surfaces.

The results from these calculations are presented in Figure 1 and Table V. Positive values of E_{form} indicate that formaldehyde is lower in energy than H₂ and CO.

Figure 1 demonstrates that ΔE_{form} depends exponentially on core overlap, similarly to E_{t-h} . Increasing the core radii lowers both ΔE_{form} and E_{t-h} , although the range of ΔE_{form} values is larger than the range of E_{t-h} values. We find a converged ΔE_{form} of 0.55 eV, considerably overestimating the experimental ΔE_{form} of 0.30 eV. Thus we see that DFT/GGA calculations fail for a variety of calculations involving the CO molecule.

IV. ACCURACY OF THE CHEMISORPTION ENERGY AT THE TOP AND HCP SITES

Since E_{t-h} is the difference of two binding energies, error in E_{top}^{chem} and/or E_{hollow}^{chem} can lead to a wrong E_{t-h} . We now consider how the chemisorption error varies with site. For quarter monolayer coverage, our converged E_{chem}^{top} is 1.729 eV. This agrees well with the experimental adsorption energy of 1.68 ± 0.12 eV obtained by Yeo *et al.*¹⁵ for the CO/Pt(111) system at $\Theta = 0.25$, where CO molecules are adsorbed mostly on the top sites⁸, with only a small bridge site population. The hcp binding energy at quarter coverage is not known, but it must be smaller than the adsorption energy at the top or bridge sites. The experimental difference between E_{chem}^{top} and E_{chem}^{bridge} is estimated to be about $0.06 \text{eV}^{2,38,39}$. Since the bridge site is populated at low coverages, while the hcp site is not, E_{chem}^{hcp} must be smaller than E_{chem}^{bridge} . Therefore, E_{chem}^{hcp} is at most 1.63 ± 0.12 eV. Our converged value for E_{chem}^{hcp} is 1.811 eV.

TABLE V. Results of DFT-GGA calculations for the reaction $H_2 + CO \rightarrow H_2CO$ reaction for various carbon and oxygen pseudopotentials. PSPs 1-5 were created with 81 Ry plane-wave cutoff, and PSPs 6,7 were created with 50 Ry plane-wave cutoff. Shown are the CO bond energy (BE_{CO}) , CO bond length (R_{CO}) and the energy of the reaction (E_{form}) . The CO bond length in formaldehyde is shown in parenthesis. All experimental results taken from the CRC Handbook⁴⁴, unless otherwise noted. Energies are in eV, core radii are in a_0 and bond lengths are in Å.

	$r_c^{ m O}, r_c^{ m C}$	$BE_{\rm CO}$	$R_{ m CO}$	$E_{\rm form}$
	(a_0)	(eV)	(Å)	(eV)
PSP 1	0.50,0.58	11.758	1.150(1.221)	0.546
PSP 2	0.58, 0.64	11.835	1.149(1.220)	0.550
PSP 3	0.64, 0.69	11.836	1.147(1.219)	0.538
PSP 4	0.69, 0.74	11.881	1.144(1.217)	0.528
PSP 5	0.74, 0.79	11.967	1.142(1.213)	0.512
PSP 6	0.74, 0.79	12.200	1.142(1.201)	0.512
PSP 7	0.79, 0.85	12.409	1.122(1.193)	0.424
AE		11.660^{42}	$1.136^{37} (1.209)^{43}$	0.46^{43}
Exp		11.27	1.128(1.210)	0.30^{43}

We see that the $E_{\text{chem}}^{\text{top}}$ is overestimated by about 0.05 eV, while $E_{\text{chem}}^{\text{hcp}}$ is overestimated by at least 0.18 eV. Since the $E_{\text{chem}}^{\text{top}}$ is within the experimental error bars, we conclude the wrong $E_{\text{t-h}}$ is due primarily due to the erroneous value $E_{\text{chem}}^{\text{hcp}}$. This demonstrates that for CO on Pt(111), DFT-GGA methods give significant error for adsorption on the hcp site, but the top site is treated accurately. We will now address the cause of DFT-GGA failure.

V. BONDING CONTRIBUTIONS TO CHEMISORPTION SITE PREFERENCE

Since DFT-GGA is inaccurate in a similar way for a variety of CO/metal systems and an organic reaction, we investigate whether there is a common reason for this failure. To understand the causes of DFT-GGA failure, first consider the nature of E_{t-h} .

The site preference energy E_{t-h} is the difference in the chemisorption energies of the CO molecule on the two surface sites.

$$E_{\rm t-h} = E_{\rm top} - E_{\rm hollow} \tag{1}$$

 E_{t-h} is also the energy of CO migration from the top site to the hollow site, in which the CO bond is weakened, C–Pt bonds are formed and the platinum surface atoms rearrange to accommodate the CO. We can therefore write the ΔE of the reaction as the sum of energies of bonds broken and bonds formed.

$$E_{t-h} = \Delta E_{t-h}^{CO} + \Delta E_{t-h}^{C-Pt} + \Delta E_{t-h}^{Pt-Pt}, \qquad (2)$$

where ΔE_{t-h}^{CO} is the difference in CO bond energy when adsorbed on top and hcp sites, ΔE_{t-h}^{C-Pt} is the difference between bond energies of the lone C–Pt bond on the top site and the three C–Pt bonds on the hollow site, and ΔE_{t-h}^{Pt-Pt} is the energy cost of rearrangement of the Pt–Pt bonds.

To correctly predict the site preference energy, DFT calculations must either treat all bonds in Eq. 2 accurately or have the errors in various terms fortuitously cancel out. The CO/Pt(111) system is very challenging, since metals exhibit diffuse metallic bonding while the CO molecule is an example of very tight, covalent bonding. The accuracy of LDA and GGA calculations is known to diminish as the electronic charge density becomes more inhomogeneous, so the CO, metal-metal and metal-carbon bond energies will not be estimated with the same accuracy. Once the nearly perfect error cancellation is lost, a significant error in one bond energy that is not matched by an error in another bond energy will lead to a wrong E_{t-h} . Similarly, the formaldehyde formation reaction involves changing the CO bond from a triple bond to a double bond, breaking of the H_2 bond, and forming two C– H bonds. In order to compute the formation energy, these bonding changes must all be modeled accurately or with errors that cancel.

VI. BOND-ORDER CHANGES AND DFT-GGA ACCURACY

In practice GGA does not perform equally well for the energetics of all these bonds. DFT-GGA calculations are almost always very good for geometry optimization, due to the fact that the inhomogeneity of the electron gas does not significantly change as bonds shorten or lengthen slightly. Thus, the errors due to the use of an approximate functional cancel out. However, in calculating the energy difference of structures with different inhomogeneities, the error cancellation will not work as well⁴⁰. In chemical language, this change in the character of the inhomogeneous electron gas between reactants and products is known as bond order change.

The effect of bond order change on the accuracy of DFT energies can be seen from the work of Kurth *et al.*, who recently examined the performance of various exchange-correlation functionals, LDA, GGA and meta-GGA⁴¹ on atomization energies of small molecules⁴². They performed all-electron calculations, so deviations from experiment in the values of the atomization energies are due to functional error only. We show their data for LDA, PBE, RPBE and PKZB functionals in Table VI. Since we want to evaluate the quality of DFT ΔE results for reactions with molecular reactants and products, we are more interested in the accuracy of atomization energy (or bond energy) differences, than in the errors in atomization energies themselves.

From the data of Kurth *et al.*, it is clear that XC functionals perform well on bond energy differences with similar bond order, e.g. a C–H bond and an N–H bond. The energy differences between bonds of different bond order, e.g CO and NO, are considerably less accurate. To illustrate this, we plot the PBE error in bond energy in Figure 2. Inevitably, a few bond energies have very similar error differences, such as CO - C=C. However, all the energy differences between bonds of different bond order involving oxygen have large errors. The CO - NO energy difference error is 0.413 eV, and the CO - O₂ error is 0.596 eV, twice as large as the CO - N₂ error of 0.226 eV, and almost an order of magnitude larger than the CH - OH error of 0.0510 eV. The high quality of single bond energy results and the decrease in bond energy error from the double bond region to the triple bond region in Figure 2 implies that PBE calculations are accurate for first-bond energies, significantly overestimate the second-bond energies, and underestimate the energy of third bonds. Therefore, significant bond order changes are accompanied by large DFT errors. The inaccuracy of DFT in computing the relative energies of systems with different bond orders has also been noted by Mitas in his work on silicon clusters.⁴⁰

VII. THE CAUSE OF DFT-GGA FAILURE

We can now examine the source of E_{t-h} discrepancy in the CO/Pt(111) system. In Eq. 2, three terms contribute to E_{t-h} : ΔE_{t-h}^{CO} , ΔE_{t-h}^{C-Pt} and ΔE_{t-h}^{Pt-Pt} . The Pt–Pt bond order changes little from top site chemisorption to hcp site, and DFT is known to do well on metallic systems, so we rule out these bonds as a source of E_{t-h} discrepancy. The calculations of Feibelman *et al.* (Table II) show a C–Pt frequency of 461 cm⁻¹ for the top site, 393 cm⁻¹ for the bridge site, and 342 cm⁻¹ for the hollow site. The DFT results compare very well with experimental values of 466 cm⁻¹ for the top site and 385 cm⁻¹ for the bridge site. Since the top-bridge C-Pt bond order change is similar to the bridge-hcp C-Pt bond order change, and both the top and the bridge C-Pt DFT frequencies are of high quality, this suggests that the hollow site frequency is likely to be accurate as well. The calculated DFT C–Pt distances are accurate within 0.02 Åfor both sites. The high quality of frequency and bond length results implies that the C–Pt bond energies at both sites are accurate as well. Thus, there is at most a small error in the ΔE_{t-h}^{C-Pt} .

Turning to the CO bond, the experimental CO stretch frequencies (Table II) show significant chemical changes due to migration from the top to the hollow site. The CO bond at a top site is only slightly weaker than the gas-phase CO triple bond, while the CO bond on the hollow site is closer to a gas-phase CO double bond than to a triple bond. The free CO molecule has a vibrational frequency of 2140 cm⁻¹, the HCO radical CO stretch frequency is 1865 cm⁻¹, and a typical double bond CO stretch has a frequency of about 1700 cm⁻¹ in organic molecules. The experimental top site CO stretch frequency in the CO/Pt(111) system is 2095 cm⁻¹, the bridge site CO stretch frequency is 1845 cm⁻¹, and the hollow site frequency can be estimated at around 1770 cm⁻¹²⁹. Molecular orbital analysis assigns the gas-phase CO a bond order (BO) of 3, HCO BO = 2.5 and C=O BO = 2. Interpolation based on vibrational frequencies allows us to estimate the top site CO BO = 2.9 and hollow site CO BO = 2.2. This implies a rather significant CO bond order change of 0.7. Since, as shown by the results of Kurth *et al.*, PBE underestimates the energy of the third CO bond, the energy cost of CO bond order change from 2.9 to 2.2 will be underestimated. This will lead to an overestimation of the E_{chem}^{hcp} and consequently to the incorrect E_{t-h} . In the same fashion, the underestimation of the energy cost of the third CO bond breaking will lead to an overestimation of the energy cost of the third CO bond breaking will lead to an overestimation of the energy cost of the third CO bond breaking will lead to an overestimation of the energy cost of the third CO bond breaking will lead to an overestimation of the energy cost of the third CO bond breaking will lead to an overestimation of the energy cost of the third CO bond breaking will lead to an overestimation of the energy cost of the third CO bond breaking will lead to an overestimation of the energy cost of the third CO bond breaking will lead to an overestimation of the energy cost of the third CO bond breaking will lead to

A comparison of our converged top and hollow site chemisorption energies supports the assignment of DFT failure to the CO bond. As shown above, the E_{top}^{chem} value is accurate within the experimental error bars, while E_{hcp}^{chem} is off by at least 0.18 eV. The CO bond is only slightly weakened upon adsorption in the top site, as shown by experimental red-shift of only about 50 cm⁻¹ from the gas-phase CO stretch frequency and a bond order change of 0.1 from the free CO. Therefore, the accurate value for E_{chem}^{top} can be considered the result of very good DFT-GGA error cancellation in CO bond energetics. For the hcp site, with a red-shift of about 390 cm⁻¹ and CO bond order change from 3.0 to 2.2, the inaccurate chemisorption energy coincides with more dissimilar CO bonds.

The identification of ΔE_{t-h}^{CO} underestimation as the major cause of site preference error is also supported by the vibrational frequency results of Feibelman *et al.* The DFT calculations show a shift of 214 cm⁻¹ in CO bond stretch frequency from top to bridge site, and a shift of 308 cm⁻¹ from top to hcp site. These results are lower than the experimental 250 cm⁻¹

	Exp.	LDA	PBE	RPBE	PKZB
		Error	Error	Error	Error
H_2	4.76	0.16	-0.21	-0.17	0.22
CH_4	18.23	1.87	-0.03	-0.39	0.08
NH_3	12.93	1.74	0.19	-0.18	0.06
ОН	4.63	1.77	0.14	-0.01	0.06
$\rm H_2O$	10.10	1.49	0.08	-0.25	-0.10
HF	6.12	0.93	0.05	-0.14	-0.09
СО	11.27	1.73	0.42	-0.06	-0.14
N_2	9.94	1.69	0.63	0.18	0.03
NO	6.65	1.99	0.82	0.38	0.24
O_2	5.24	2.37	1.01	0.56	0.47
C_2H_2	17.63	2.38	0.38	-0.22	-0.19
C_2H_4	24.46	3.06	0.39	-0.35	-0.05

TABLE VI. Results of all-electron DFT calculations of Kurth $et \ al.^{42}$ for atomization energies of small molecules with various exchange-correlation functionals. All energies are in eV.

shift from top to bridge and the 325 cm^{-1} shift from top to hcp site. Since stronger bonds will usually have higher vibrational frequencies, this underestimate of the frequency shift provides additional evidence that GGA underestimates the energy cost of the third CO bond breaking.

VIII. CONCLUSION

We have shown that for molecule-surface systems, converged PSP calculations and allelectron calculations yield very similar results. The frozen core creates only a minimal inherent error, but core radius overlap can lead to larger deviations. An examination of the literature shows that DFT energy errors are not limited to CO adsorption on (111) metal surfaces, but occur for many reactions involving CO. We have also shown that the underestimation of CO bond energy loss in migration from the top to the hollow site is largely responsible for the incorrect site preference obtained by DFT-GGA calculations. The dependence of DFT error on bond order change implies that the top site chemisorption energy obtained by DFT-GGA calculations is accurate, while the chemisorption energy of the hollow site is not and leads to incorrect E_{t-h} . This is confirmed by our converged PSP-DFT results for E_{chem}^{top} and E_{chem}^{hcp} . Since $\Delta E_{triple-double}^{CO}$ is independent of metal surface, errors in this energy will affect the E_{t-h} site preference energies on many metal surfaces. We therefore propose that a simple empirical correction, based on reaction energies of small organic molecules, may permit accurate prediction of site preference.

Similar errors will also be found for other small molecules which experience changes in molecular bond order. The PKZB meta-GGA functional⁴¹ may predict the right site preference without empirical corrections, due to its superior performance in calculating the atomization energies of small molecules.

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FIG. 1. H₂CO and CO/Pt(111) PSP convergence. Circles correspond to site preference ΔE . Squares correspond to ΔE of formaldehyde formation. × marks the Feibelman *et al.* LAPW result for site preference ΔE .



FIG. 2. PBE error in bond energies from calculations on small molecules.