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The CO/Pt(111) puzzle

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Notwithstanding half a dozen theoretical publications, well-converged density-functional calculations, whether based on a local or generalized-gradient exchange-correlation potential, whether all-electron or employing pseudopoten-

tials, underestimate CO's preference for low-coordination binding sites on Pt(111) and vicinals to it. For example, they imply that CO should prefer hollow- to atop-site adsorption on Pt(111), in apparent contradiction to a host of low temperature experimental studies.

I) Introduction - Numerous surveys[1] support the expectation that properties of gas-phase molecules will be qualitatively, and in many cases quantitatively faithful to nature when calculated via Density Functional Theory[2] (DFT) in the Generalized Gradient Approximation[3] (GGA). Much less information is available regarding molecules and molecular fragments adsorbed on or scattering from surfaces, but the sense of the literature is certainly that the GGA provides a reliable way to analyze and interpret surface chemical phenomena.[4]

We show, nevertheless, that for a representative, and seemingly unexceptional adsorption system, the DFT potential energy surface misses significant, *qualitative* details. Specifically, we compare site preferences predicted by a variety of state-of-the-art total-energy methods to the considerable experimental information base available for CO adsorbed on Pt(111) and surfaces vicinal to it.[5-16] The result is definitive evidence that DFT underestimates CO's preference for low-coordination sites. This is true whether one employs the Local Density Approximation[17] (LDA) or the GGA,[3] and also whether the calculations are pseudopotential-based or all-electron. For example, contradicting a host of experimental studies,[5-9,13-16] all our calculations agree that at low coverage CO prefers hollow-site- to atop-adsorption on Pt(111).

An important motivation for the present report is to correct the published theoretical literature concerning CO binding on Pt(111). Several articles say or imply that DFT favors adsorption in atop sites as experimentally-observed.[18-23] Most likely, though, it takes an insufficiently flexible basis set, or perhaps too small a cluster model of the surface, to arrive at this conclusion. Making use of modern, efficient total-energy algorithms and powerful computers, and thereby eliminating convergence as an issue, we find a general preference for adsorption in higher- as against lower-coordination geometries.

Since our DFT predictions contradict scanning-probe, diffraction and spectroscopic observations,[5-16] it is hard, if not impossible, to argue that the DFT results are "right," while something is inconsistent, perhaps contamination, in the experiments. The alternative, however, is to accept that DFT is not generally trustworthy for the analysis of surface chemical processes. In that case, while awaiting an improvement on current total energy methods, it would be helpful to learn what characteristics distinguish systems or properties that current DFT describes poorly from those it describes well.

In addition to adsorption on perfect Pt(111) terraces, we report DFT-optimal CO adsorption sites for surfaces vicinal to Pt(111). They include Pt(221) on which monoatomic "B-type" steps, or (111)-microfacets, are separated by (111) terraces four atomic rows across, and Pt(322), "A-type" steps, or (100) microfacets, are separated by (111) terraces 5 atomic rows wide.

In agreement with previous DFT calculations,[32] we find that for A-steps, with CO-coverage ranging from one molecule per step-edge Pt down to one per 3 step-edge Pt's, both the GGA and the LDA predict a preference for CO in 2-fold rather than 1-fold sites. On B-type steps, the GGA predicts very small binding energy differences (~0.01 eV) for 1- vs. 2-fold sites, while in the LDA 2-fold sites are clearly preferred (by as much as 0.14 eV at the lowest coverage). These results contradict spectroscopic and scanning probe studies according to which only 1-fold step edge sites are occupied by CO at the lowest coverages.

Calculations at our several laboratories were performed independently, using different DFT computer codes. We report results for a variety of exchange-correlation potentials. We have estimated corrections for zero-point motion, entropy and spin-orbit coupling. We have performed spin-polarized calculations to see if local magnetic effects could be important. We have also checked whether the discrepancy between theory and experiment can be explained by surface defects whose thermal abundance is affected by the presence of CO.

In the end, we conclude that DFT calculations cannot yet be viewed as a "black box" simulation tool. Before DFT results can be compared to experiment, particularly when energy differences are small, one needs not just to assess numerical convergence, but also to re-examine the quality of various approximations, e.g., the pseudopotential version of the electron-nucleus interaction and the choice of exchange-correlation functional. Even then, though, as we find for CO/Pt(111), successful prediction of adsorption sites is not guaranteed.

On the positive side, incorrectly predicted adsorption-site preferences do not *necessarily* imply poor predictions of surface chemical phenomena.[4a-c] Moreover, our present finding that site-preference energies are improved, if one uses the RPBE version of the GGA exchange-correlation potential,[4a] offers hope that a sufficiently improved GGA will soon allow potential energies for molecules on surfaces to be predicted with confidence.

In the next sections of this article we review the experimental (Sec. II) and the theoretical (Sec. III) literature that bears on the geometry of CO adsorbed on Pt(111) and vicinals. In Sec. IV, we describe the several DFT methods we have employed to compute CO bonding geometries. We present extensive results in Sec. V, and discuss the lack of agreement with experiment in detail. In Sec. VI, we estimate corrections that one might hope would improve agreement with experiment. Finally, we devote Sec. VII to a discussion of key questions: Is the DFT error in site-preference energies "big?" Is it "surprising?" And finally, can we identify its source by comparing prediction and observation for CO on other close-packed metal surfaces?

II) Experimental CO bonding geometries on Pt(111) and its vicinals - The geometry of CO on stepped and perfect Pt(111) has been studied by using diffraction, vibration spectroscopy and scanning probe microscopy. In what follows, we provide a representative sample of the results.

A) LEED measurements: Structures of CO/Pt(111) based on Low Energy Electron Diffraction (LEED) analysis have been reported by D. F. Ogletree, M. A. Van Hove and G. A. Somorjai[5] (OHS) and by Blackman, et al..[6] OHS examined the c(4×2)-CO/Pt(111) structure at 150K and found that in each unit cell there is one CO 1-fold coordinated at an atop site and another, 2-fold coordinated in a bridge geometry. Blackman et al. studied a disordered one-third monolayer of CO on Pt(111) at 160 K, and found that (88±5)% of the molecules occupy atop sites while (12±5)% are at bridge sites.

B) Vibration spectroscopic measurements: According to the Low Energy Electron Diffraction (LEED) and Electron Energy Loss Spectroscopy (EELS) results of Hopster and Ibach,[7] and of Steininger et al.,[8] CO adsorbs at low coverage in a $\sqrt{3}\times\sqrt{3}$ - R30° structure and resides in atop sites. The latter report concludes that at saturation, the structure converts to c(4×2) with a half bridge, half atop geometry.

Schweizer et al.[36] actually determine an empirical potential energy surface for CO/Pt(111). They do this via a fit to their infrared measurements of the CO stretch frequency and width vs. coverage and temperature. Extrapolating to zero coverage, they conclude that binding at the atop site is preferred by ~60 meV relative to the bridge. They observe no absorption line corresponding to adsorption in a 3-fold hollow.

B. Hayden, et al.[9] judge from Infrared Absorption Spectroscopy (IRAS) on the (100)-microfacet steps of Pt(533) that CO preferentially resides at step-edge 1-fold sites. Using EELS instead, Luo, et al.[10] come to the same conclusion for CO-coverages up to 0.12ML. Beyond that, the population of edge-bridge sites increases rapidly. Then terrace atop sites are occupied, followed by terrace bridges. This sequence is confirmed in the IRAS experiments of Xu and Yates.[11]

In earlier work Henderson, et al.[12] showed via LEED that below 0.19ML coverage on Pt(211), a surface with A-type steps separating (111) terraces three atomic rows across, CO adsorbs in step-edge sites separated by two Pt-Pt spacings. Their electron Stimulated Desorption Ion Angle Distribution (ESDIAD) analysis then confirms that as on CO/Pt(533), the CO resides in 1-fold edge sites on Pt(211) at these coverages.

C) Scanning probe microscopy measurements: Bocquet and Sautet's[13] (B&S's) theoretical simulations of Scanning Tunneling Microscopy (STM) imply that atop-bound CO should image as a prominent "bump" on Pt(111) and bridging CO as a "sombrero." CO in a hollow site should produce a relatively flat bump surrounded by a rather deep depression. B&S thus infer that Stroscio and Eigler's STM pictures of CO/Pt(111) show atop and bridge CO's but none in hollows.[14] Similarly, Pedersen, et al.[15] compare simulations for five possible c(4×2) arrangements of CO/Pt(111) to STM images. They conclude that half the CO's are in atop sites and half at bridges. Gambardella[16] has obtained 77K images of CO/ Pt(997), a vicinal with (111)-microfacet steps, in which the corrugation associated with Pt atoms is sufficiently resolved that one can plausibly identify the positions of step-adsorbed CO molecules. The molecules appear to be preferentially adsorbed in 1-fold edge sites.

The overall conclusion is that CO prefers coordination to a single Pt atom, at low coverage. On the other hand, since Stroscio and Eigler observe *two* sites occupied on Pt(111) at 4K, there can be only a small energy difference between atop binding and binding in the next most favorable site, the bridge according to B&S. Consistent with this conclusion, the atop-bridge configuration is preferred at high coverage; but again in that case, according to Schweizer et al.'s empirical analysis,[36] the effective atop vs. bridge binding-energy difference is on the order of tens of meV, depending on coverage. The corrugation of the CO/Pt(111) potential energy surface is thus relatively weak. Calculating it accurately is accordingly a stringent test of one's numerical and physical approximation scheme.

III) Previous theoretical DFT geometries of CO on Pt(111) - Both cluster and slab-model DFT bonding geometries have been published for CO on Pt(111). In some papers, binding energies computed for different sites lead to the conclusion that atop bonding is favored over bridge and bridge over hollow. In other work it is simply assumed that the atop site is most favorable. As we now enumerate, however, *none* of the published DFT results agrees with our converged calculations:

A) <u>CO adsorption on Pt(111) slabs</u>: Philipsen, et al.[18] say that a scalar relativistic GGA calculation shows a roughly 0.24 eV preference for the atop site relative to the *hcp* hollow. Adding the effect of spin-orbit coupling lowers the binding energy in both sites, but the difference remains the same. These calculations, for a 2-layer Pt film in a $\sqrt{3}\times\sqrt{3}$ - R30° geometry, use a small localized basis set including numerical and slater-type functions. The reason for focusing on the *hcp*, rather than the *fcc* hollow is not explained in Ref. 18, but cannot make a difference nearly large enough to affect the conclusion that atop bonding is favored. Hammer, Morikawa and Nørskov[19] report agreement to ~3% with experiment for binding energy and to ~1% for CO-stretch vibration frequency with CO in an atop site, but they only performed calculations for this binding configuration. In their DFT study of CO oxidation on Pt(111), Alavi, et al.[20] also assume that CO is initially adsorbed in atop sites. In unpublished calculations with the O adatoms, but not the CO admolecules, removed from their p(2×2) supercell, one of the authors of Ref. 20 finds that the most favorable CO adsorption site is the *hcp* hollow, with the binding energy 0.11 eV larger than for the least favorable symmetry site, that is, the atop site.[24]

B) CO adsorption on Pt(111) clusters: Using a localized basis set and the LDA, Jennison, Schultz and Sears[21] consider "1/4 ML" CO on a large cluster, with Pt atoms frozen in bulk relative positions. They find that the CO prefers atop adsorption by "several tenths of an eV," compared to hollows or bridges. In Curulla, et al.'s GGA calculations,[22] bridge bonding is about 0.9 eV lower in binding energy than the atop site, for a 25 atom "Pt(111)" cluster. An LDA calculation by Ohnishi and Watari[23] leads to the conclusions that atop bonding is preferred to bridge by 1.1 eV on Pt(111), and that CO is not bound at all in hollow sites.

Thus, all published DFT calculations of the adsorption geometry of CO on Pt(111) either predict or assume the experimental "right answer." But, as documented in the sections that follow, well-converged DFT calculations do not.

IV) DFT methods used in the present work - Aiming to eliminate any doubt that DFT predicts binding geometries in conflict with experiment for CO adsorbed on Pt(111) or a step on this surface, we report results here obtained in several laboratories using different, independently-written computer codes. In all our calculations, we use plane-wave (or augmented plane-wave) orbital sets, systematically improved till convergence is achieved. We represent Pt(111) and its vicinals by slabs from four to six Pt(111) layers thick., again testing to confirm convergence.

Results of our various calculations are presented and discussed in detail in the next section. Here, first, we briefly review the methods used to obtain them:

A) VASP calculations - The Vienna *Ab-initio* Simulation Package[25-27] (VASP) represents electron-ion-core interactions either via ultrasoft pseudopotentials (USP's)[28] or Blöchl's Projector Augemented Wave (PAW) approach.[29] We report results for both. In certain cases we also compare energies based on the Ceperley-Alder version of the LDA[30] and the Perdew-Wang '91 (PW91) GGA.[3]

The PAW and USP methods yield converged total energy differences with modest plane-wave basis size. In the present case, the minimum acceptable basis cutoff is fixed by the presence of O atoms. We use ~29 Ry.

Adsorption energies in the tables correspond to periodic arrangements of CO on thin Pt slabs whose bottom layers are clean and fixed in a geometry corresponding to bulk, DFT Pt [lattice parameter = 3.989Å (GGA), 3.911Å (LDA)]. At least two upper Pt layers are allowed to relax in response to the presence of the CO. To accelerate electronic relaxation, we use Methfessel and Paxton's Fermi-level smearing method (width = 0.2 eV).[31]

B) Dacapo calculations - The "Dacapo" pseudopotential code, developed at CAMP, Denmark,[4] allows for USP calculations with a range of different exchange-correlation approximations. Here we include results with the well-known local LDA[30] and non-local PW91[34] approximations and the more recent non-local PBE[35] and RPBE[4] approximations. The PBE functional is a simplified version of the PW91 functional,[3] and the RPBE functional is a revised version of the PBE functional, in which the exchange enhancement factor has a different mathematical shape. The PBE and the RPBE functionals obey the same set of physical constraints and share the same values of all parameters.

For the electronic states we employ a basis consisting of plane waves with kinetic energy below 25 Ry. Electronic energy levels are populated according to a Fermi-Dirac function at kT=0.1 eV. Slabs of 6 Pt layers are decorated by CO on one side in p(2x2), c(4x2) and $\sqrt{3}\times\sqrt{3}$ - R30° patterns. The adsorbates and the upper three Pt layers are completely relaxed. Lattice constants are chosen consistent with the exchange-correlation approximation used [LDA: 3.93 Å, PW91, and PBE: 4.00 Å, RPBE: 4.02 Å, but e.g. the RPBE results are almost unchanged when evaluated at the PW91 lattice constant. The pseudopotentials used include core contributions with cutoff radii of $r_c^C = 0.6$ bohr, $r_c^O = 0.7$ bohr and $r_c^{Pt} = 1.2$ bohr.

C) FP-LAPW calculations – In our full-potential, linearized augmented-plane wave (FP-LAPW) calculations, we used the "WIEN" code,[37] which was developed at the Technical University of Vienna, then improved[38-40] at the Fritz-Haber-Institut. This code allows very accurate all-electron calculations using several different approximations for the exchange-correlation functional (LDA,[30] PW91,[3] PBE[35]).

For example, to ensure high accuracy in the calculations reported below, we treat Pt 5s and 5p (semi-core) states using the local-orbital extension[41] of the LAPW-basis, and treat the core fully relativistically, i.e. solving the Dirac equation. For semi-core and valence states we report both scalar-relativistic (REL) and non-relativistic (NREL) results.

"Technical" parameters of the FP-LAPW calculations were carefully checked for convergence. The values finally used are given in Table I. In order to improve the stability of the electronic convergence we populate orbitals consistent with electronic temperature kT^{el} =0.13 eV. Then we extrapolate the computed total energy to its $T^{\mathrm{el}} = 0$ K value.[42,43]

Calculated bulk lattice parameters for various exchange-correlation (XC) functionals and treatments of relativistic effects are given in Table II. We model the Pt(111) surface by a 5-layer slab, setting the substrate lattice constant to the theoretical bulk value for the appropriate XC-functional and treatment of relativity (cf. Table II), and adsorbing CO on both its top and bottom surfaces in a $\sqrt{3}\times\sqrt{3}$-R30° geometry. Tests with a 7-layer slab do not show a significant change in energy differences. In the studies reported below, we took the lateral position of the carbon atom (*X, Y*) as a reaction co-ordinate and calculated the full potential energy surface, *E(X, Y)*, by relaxing all other CO coordinates as well as the top two Pt layers.

V) New DFT results for CO adsorbed on Pt(111) and vicinals - Here we report binding-site preference energies calculated for various coverages of CO on perfect and stepped Pt(111) surfaces, using the DFT approaches described in the foregoing section:

CO coverage up to 1/3 ML on Pt(111) - At coverages =1/3ML, CO is found experimentally to reside preferentially in atop sites on Pt(111).[5-9,14] Our lowest coverage calculations (cf. the summary in Table III) are for 1/12ML CO/Pt(111), with one CO per $3\times2\sqrt{3}$ supercell at an atop or an *fcc*-hollow site on a six-layer Pt(111) slab. In these calculations, we fix the Pt atoms of lower three slab layers in bulk-Pt relative positions (using the DFT lattice parameter) and sample the full SBZ with 4×4 **k**-point mesh. The CO binding energy for the atop case is 0.25 eV less than for the hollow site.

We show in what follows that this energetic preference for the "wrong" site, i.e. the *fcc* hollow, is characteristic of the low coverage regime. Using any one implementation of DFT, such as GGA with USP's, predicted binding site preferences vary only weakly with coverage (VASP) or not at all (Dacapo), up to 1/3 ML of CO.

For 1/4ML coverage, we consider CO adsorption with two different periodicities, p(2×2) and c(4×2), via calculations based on the LDA and various embodiments of the GGA. We also compare USP's for this coverage to the PAW method. The universal conclusion is that DFT favors *fcc*-hollow bonding over the atop site. Among the GGA results, the energy by which the 3-fold hollow is prefered varies between 0.13 and 0.24 eV, depending on details. Within the LDA, the preference for the 3-fold hollow is ~0.4 eV.

To be more specific, the VASP-USP and VASP-PAW calculations for c(4×2)-CO/Pt(111) again are for 6-layer slabs whose lower three layers are fixed in bulk positions (PAW and USP lattice parameters are found to be virtually identical) while the remaining atoms allowed to relax freely. A 4×4 sample of the full SBZ yields energy preferences that differ by about 1% from those for a 6×8 sample of equally spaced k-vectors. A PAW calculation in which the plane-wave cutoff is increased from ~29 to ~51Ry reduces the predicted *fcc* vs. atop preference to 0.13 eV from 0.15 eV. The USP result for the ~29Ry cutoff is 0.18 eV, in modest agreement with the PAW calculation for the same basis cutoff.

The VASP-USP preference for the *fcc* site is much larger in the LDA, 0.41 eV, in good agreement with the Dacapo-USP LDA calculation for p(2×2)-CO/Pt(111), which yields ~0.45 eV. The Dacapo calculations, whether based on the LDA or one of several GGA exchange-correlation potentials (see Table III) were for six-layer

Pt(111) slabs of which the atoms of the bottom three layers were held fixed in bulk DFT relative positions. In these calculations, the SBZ's corresponding to p(2x2), c(4x2) and $\sqrt{3}\times\sqrt{3}$ - R30° surface unit cells were sampled via 18, 16, and 54 **k**-points.

Note that the Dacapo results based on the PW91 and PBE versions of the GGA are in close agreement with each other, as might be expected. On the other hand, if one uses the RPBE potential, which is found to represent the absolute CO binding energy more accurately than PBE or PW91, the energy preference for the fcc hollow is reduced by about 33%. Noting that use of the PAW method in place of USP's reduced the *fcc* energy preference by a comparable percentage, one may imagine that PAW calculations based on the RPBE XC-potential would produce the desired result that the atop site is favored. Whether proceeding down this path will lead to a robust DFT methodology is not known at this point.

Our LAPW calculation for the 1/3 ML, $\sqrt{3}\times\sqrt{3}$-R30° structure predicts only a 0.10 eV preference for the *fcc* hollow. This all-electron calculation was performed for CO adsorbing on both sides of a 5-layer film, while the SBZ was sampled with 6 equally spaced k-vectors. Tests using a 7-layer slab and 24 SBZ sampling vectors produced virtually the same results. As in the 1/4ML comparison between USP and PAW results, here the Dacapo-USP calculation yields a larger site preference energy than the LAPW. The reason for the reduced corrugation of the CO potential in the all electron calculations is a matter worth pursuing, with the prospect in mind that if their corrections to the corrugation of the CO/Pt(111) potential are additive, RPBE-based, all-electron calculations might produce the experimentally observed preference for low-coordination sites.

c(4×2)-2CO/Pt(111) - Both STM[15] and LEED[8] studies of the half-monolayer c(4×2)-2CO/Pt(111) structure imply that in each unit cell there is one CO in an atop site and one at a bridge (and *none* at a hollow!). For comparison, therefore, we performed GGA calculations, using the VASP-USP and DACAPO-USP approaches, for the five CO-binding arrangements considered in the STM study, again modeling the Pt surface with a 6-layer slab. These calculations were performed using the same slab and SBZ sample as in for the c(4×2)-CO/Pt(111), 1/4 ML case.

The results summarized in Table IV indicate that within the PW91 GGA, the difference between the best pair of CO sites (*fcc* and *hcp*) and the worst (atop and bridge) is rather small, only 10 to 20 meV/CO. But it is still in the wrong direction, i.e., the PW91 GGA predicts that both CO's per cell should reside in 3-fold hollow sites at 0K. On the other hand, if the RPBE functional[4a] is used, occupying the correct, atop and bridge sites is favored, a hopeful indication.

CO on steps - On a Pt(111) surface there are two types of straight step, commonly called A- and B-type steps, that differ by having (100)- and (111)-microfacet risers. We estimate binding energies for CO on such steps, via VASP-USP calculations of CO on Pt(322) and Pt(221) thin slabs. The Pt(221) surface has (111) terraces 5 atomic rows across, separated by A-type steps. The Pt(322) has (111) terraces 4 atomic rows wide separated by B-type steps.

The vicinal slabs used to model step-adsorption are between four and five (111)-layer separations thick. The atoms corresponding to the lower two (111) layers of the slabs are held fixed in bulk DFT positions and all others are permitted to relax. To learn how binding preference depends on coverage, we compute total energies for hypothetical ordered arrangements of CO step-coverages of 1/3, 1/2 and 1 CO per step-edge Pt atom, at either 1- or 2-fold edge sites. The SBZ for the lowest step coverage is sampled by a 2×2 array of equally spaced k-vectors. For half step coverage, we use a 4×4 SBZ sample and when there is one CO per edge Pt atom, we use an 8×4 SBZ sample.

The calculations are performed within both the LDA and the GGA. The results, summarized in Table V, show, most importantly, that at the lowest (i.e. 1/3) step coverage, CO prefers 2-fold to 1-fold step edge coordination in agreement with earlier GGA results [32]. At higher step-coverage, within the GGA, the preference shifts to 1-fold binding in the GGA calculation, but not in the LDA. Experiment, as noted above, implies that 1-fold step-edge sites are occupied first, in contradiction to the DFT results.

VI) Can these wrong results be fixed? -

We report in this section our efforts to resolve the discrepancies between the DFT predictions and experimental observations of CO binding geometries on Pt(111), considering both potential theoretical deficiencies and experimental artifacts.

CO on Pt adatoms - Since standard LEED is only sensitive to ordered surface regions, and EELS cross sections are especially large for CO adsorbed on defects (and ignoring the low-coverage STM evidence for the moment), we decided to test whether EELS observations of 1-fold bonded CO/Pt(111) might be attributable to CO attached to Pt adatoms on Pt(111). This is only possible if CO stabilizes Pt adatoms appreciably on Pt(111), because the formation energies of self-adsorbed atoms on close-packed surfaces tend to be large and adatom concentrations correspondingly small. What we find, using V*A*SP-USP, is that the CO binding energy on a Pt adatom is 40 meV higher than in an *fcc* hollow on Pt(111). This is not nearly high enough relative to 1.07 eV, the GGA formation energy computed for Pt adatoms on Pt(111), to make CO-Pt ad-trimers plentiful.

H-contamination - To see whether experiments on c(4×2)-2CO/Pt(111), for example, might have been marred by H contamination, particularly by sub-surface H, we extended our calculations by adding a H atom in each octahedral site between the first and second Pt layers. This changes the ordering of the five CO adsorption geometries we investigated. However, (see Table VI) the atop-bridge configuration does not become the most favorable. Worse, the energy cost of placing H atoms beneath the outer Pt layer is only barely compensated by the binding energy of the CO's on the surface. In other words, this configuration is only barely stable.

Relativistic corrections to CO binding energies - We undertook two different supplementary calculations in attempts to determine the effect of relativity on the CO/Pt(111) site-preference energy. Using the FP-LAPW approach, we performed fully relativistic (i.e., Kohn-Sham-Dirac equation) PW91 calculations for comparison with fully *non*-relativistic ones. The result is that the preference for fcc-hollow- vs. atop-bonding is twice as large in the non-relativistic case. To some extent, this difference is determined by the rather large lattice constant of non-relativistic, PW91 Pt, 4.22 Å (exp't=3.92 Å) as compared to the much more reasonable relativistic value, 3.99 Å.

In all other results discussed to this point, semi-relativistic but not spin-orbit corrections to the Kohn-Sham equations have been included. For a rough estimate of spin-orbit contributions to site preferences we replaced the Dacapo pseudopotential originally constructed as an appropriately weighted sum of j=l-1/2 and j=l+1/2 contributions, first by the j=l-1/2 potential then by the j=l+1/2. The difference in the 1/4 ML CO site-preference energies calculated with these two potentials was 70 meV, i.e., a relatively small energy compared to the 0.23 eV preference computed for the spin-averaged case. In both cases the fcc site remained the favored one.

The conclusion of these studies is that including all relativistic effects is not enough to produce a preference for atop-site bonding.

Spin polarization - Leaving no stone unturned, we also checked whether ad-CO on Pt(111) might be spin-polarized on Pt(111). Thus, using the VASP-PAW code, we started total energy calculations for c(4×2)-CO/Pt(111), with a spin-polarized CO in either an fcc or an atop binding site. In both cases, though, the spin moment diminishes to zero as the total energy optimization proceeds to convergence. Thus, there is *no* spin-polarization energy contribution to the site-preference energy.

Zero-point energies and vibrational entropy corrections to DFT energies - Bearing in mind Gu et al.'s [33] discovery of entropy-driven, adsorption-site changes for CO on Co($10\bar{1}0$), we have investigated how both entropy and zero-point vibration energy affect the CO site preference on Pt(111). To begin, in a $\sqrt{3}\times\sqrt{3}$-R30° supercell, we calculate the dynamical matrix, and find the normal modes for 1/3 ML CO adsorbed in atop, bridge and fcc sites on a two-layer rigid Pt(111) slab. The calculated frequencies are shown in Table VII.

Both the atop and fcc sites are local minima, while the bridge is unstable against motion of the CO molecule towards the fcc site, hence one imaginary frequency. From the calculated frequencies we can calculate the effect of zero point motions – the zero point energies are 218 and 196 meV in the atop and fcc sites. Inclusion of zero-point energies thus decreases the stability of the atop site further.

In the harmonic approximation, we also calculate the difference in entropy for the two sites. The result is that the vibrational entropy for the atop site is 0.083 meV/K higher than for the fcc site at ~300 K. This implies an entropy contribution to the free energy of about 25 meV, in favor of the atop site at 300 K. At higher T, entropy stabilizes the atop site further. On the other hand, at 4K, where the Stroscio-Eigler STM experiments were performed, the entropy contribution to the CO free energy is negligible.

VII) Discussion:

Is the DFT error in site-preference energies "big?" - At 1/12 ML, the lowest coverage for which we have performed calculations, the PW91 preference for the fcc site is 0.25 eV, relative to atop bonding. Noting that no molecule in Stroscio & Eigler's 4K STM images appears to be bound in an fcc site, the PW91 energy preference must thus be incorrect by more than 0.25 eV, a substantial error. At higher coverage, where calculated preference energies are smaller (cf., Table III), the theoretical error may also be smaller.

A similar conclusion may be drawn in comparing 0K calculated potential energy differences to site preferences observed at room temperature or above. Now it is the *free* energy that determines the preferred site, and preliminary calculations imply that the vibrational entropy contribution to the free energy favors atop bonding.

Evidently, to the extent the atop-site preference is an entropy effect, it is not the result of a potential energy difference.

Is the DFT error in site-preference energies "surprising?" - Whether a result is "surprising" or not obviously depends on expectations. Calculations of the energy needed to atomize CO can produce errors of several tenths of an eV, depending on which version of GGA exchange-correlation potential one uses.[1] Thus, it can be argued, it would be remarkable if the GGA could accurately predict a potential energy corrugation of only ~0.1-0.2 eV. On the other hand, atomization explores aspects of DFT's accuracy very far from what site preferences probe. For example, the CO molecule has a singlet ground state while the C and O atoms are triplets. This means that to produce correct atomization energies, DFT has to account faithfully for atomic spin-polarization energies. But changing the site where a CO is bound has no effect on its spin polarization -- so errors in spin-polarization energy have no bearing on site preference at all.

It is true that as a CO displaces from 3-fold to bridge to atop site the number of C-Pt bonds changes, and so does the C-O bond order. But the changes in C-O bond length in moving from one site to another are small compared to what is needed to atomize CO -- and the energy changes are similarly small compared to the atomization energy of over 11 eV. Atomizing a CO, in other words, is a very non-linear process -- there are gross changes. Moving a CO along Pt(111) is by contrast a relatively weak perturbation of the molecule. Thus it is not at all clear that calculated errors in the CO atomization energy predict errors in corrugation of the CO/Pt(111) potential energy surface.

Systematics of the binding-site discrepancy? - Pt(111) is not the only close-packed metal surface for which DFT fails to predict the correct CO binding site. On the other hand, available experimental and theoretical information (see Table VIII) does not reveal any obvious systematics. One might hope, for instance, to see that Pt(111) is an exceptional close-packed surface, with DFT correct for CO on all or most other metals, or alternately, that the problem is CO and DFT predicts binding sites incorrectly in most cases.

But insight does not leap off the page. Sautet et al.'s recent GGA calculations for CO/Pd(111) correctly predict the observed 3-fold CO binding sites. On the other hand, Lopez and Nørskov's new results for CO/Cu(111) contradict Angle-Resolved Photoemission Extended Fine Structure (ARPEFS) as well as spectroscopic analysis, which place CO in atop sites at 1/3ML coverage. Experimental observation now favors the *fcc* hollow for CO/Ni(111) after initial experimental evidence supporting occupation of 2-fold bridge sites. Binding-site calculations have not been reported for Ir(111), nor for the (0001) faces of Co, Tc, Os or Re. Experimental binding sites remain to be determined for Ir(111), Tc(0001) and Os(0001).

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Table I. Parameters of the FP-LAPW calculations: cutoff for the plane wave representation of the wavefunctions (wf) and potential (pot), cut-off for the spherical harmonics representation, and the muffin-tin radii.

E^{wf}	16 Ry
E^{pot}	81 Ry
l_{max}^{wf} (sph.)	12
l_{max}^{wf} (non-sph.)	6
l_{max}^{pot}	6
R^{MT} (Pt)	1.19 Å
R^{MT} (C, O)	0.53 Å

Table II. Theoretical lattice parameter (in Å) of fcc Platinum

core electrons	REL	REL
valence electrons	REL	NREL
LDA	3.91	4.17
PW91/PBE	3.99	4.22

Table III. Binding energy at *fcc*- relative to atop-site for low coverage CO/Pt(111)

supercell	θ(ML)	method	XC	ΔB.E.
$3\times2\sqrt{3}$	1/12	VASP,USP	PW91	0.25eV
2×2	1/4	Dacapo,USP	PW91	0.23eV
2×2	1/4	Dacapo,USP	PBE	0.24eV
2×2	1/4	Dacapo,USP	RPBE	0.16eV
2×2	1/4	Dacapo,USP	LDA	0.45eV
c(4×2)	1/4	VASP,USP	LDA	0.41eV
c(4×2)	1/4	Dacapo,USP	PW91	0.23eV
c(4×2)	1/4	VASP,USP	PW91	0.18eV
c(4×2)	1/4	VASP,PAW	PW91	0.13eV
$\sqrt{3}\times\sqrt{3}$ - R30°	1/3	Dacapo,USP	PW91	0.23eV
$\sqrt{3}\times\sqrt{3}$ - R30°	1/3	LAPW	PW91	0.10eV

Table IV. For c(4×2)-2CO/Pt(111), binding energy (in meV) vs. sites occupied by the 2 CO's in each cell, relative to atop & bridge site occupation

Adsorption sites	**VASP PW91**	**Dacapo PW91**	**Dacapo RPBE**
atop & bridge	0	0	0
atop & fcc	32	12	
bridge & fcc	16		
bridge & bridge	16		
fcc & hcp	42	15	-80

Table V. VASP-USP CO binding preferences (in eV) on straight steps

Vicinal	step type	edge-Pt's/CO	PW91 ΔBE(bridge-atop)	LDA ΔBE(bridge-atop)
Pt(322)	A	3	0.15	0.26
Pt(322)	A	2	0.15	0.27
Pt(322)	A	1	0.17	
Pt(221)	B	3	0.01	0.14
Pt(221)	B	2	-0.01	0.13
Pt(221)	B	1	-0.01	

Table VI. For c(4×2)-2CO/2H/Pt(111), assuming an H underlayer, binding energy (in meV) relative to occupation of atop & bridge sites by the 2 CO's in each cell

Adsorption sites	**XC**	**B.E.(meV)/CO**
atop & bridge	PW91	0
atop & fcc	PW91	278
bridge & fcc	PW91	-64
bridge & bridge	PW91	-76
fcc & hcp	PW91	-108

Table VII. Calculated normal mode frequencies (cm^{-1}) for CO in atop, bridge and fcc sites on a two layer Pt(111) slab. No symmetry has been assumed in the calculation. That is why modes that are degenerate by symmetry may be slightly different.

atop	2140	461	379	378	78	78
bridge	1926	393	355	316	180	imaginary
fcc	1832	342	337	332	162	154

Table VIII. Experimental vs. GGA CO adsorption-site preferences

surface	periodicity	coverage	method	site(s)
Co(0001)	$\sqrt{3}\times\sqrt{3}$ - R30°	1/3ML	LEED[a]	atop
Ni(111)	$\sqrt{3}\times\sqrt{3}$ - R30°	1/3ML	PED[b]	bridge
Ni(111)	up to c(4×2)	=1/2ML	XPS[c], PED[d]	fcc & hcp
Ni(111)	c(4×2)	1/2ML	PED,[e] LEED,[f] STM[g]	fcc & hcp
Ni(111)	**p(2×2)**	**1/4ML**	**GGA[h]**	**fcc**
Cu(111)	$\sqrt{3}\times\sqrt{3}$ - R30°	1/3ML	ARPEFS[i]	atop
Cu(111)	**$\sqrt{3}\times\sqrt{3}$ - R30°**	**1/3ML**	**GGA[j]**	**hcp**
Ru(0001)	$\sqrt{3}\times\sqrt{3}$ - R30°	1/3ML	LEED[k]	atop
Ru(0001)	disordered	=0.2ML	DLEED[l]	atop
Ru(0001)	**$\sqrt{3}\times\sqrt{3}$ - R30°**	**1/3ML**	**GGA[m]**	**atop**
Rh(111)	$\sqrt{3}\times\sqrt{3}$ - R30°	1/3ML	LEED[n]	atop
Rh(111)	p(2×2)	1/4ML	GGA[o]	hcp
Pd(111)	$\sqrt{3}\times\sqrt{3}$ - R30°	1/3ML	PED,[p] LEED[q]	fcc
Pd(111)	disordered	~0.02ML	STM[r]	fcc & hcp
Pd(111)	**$\sqrt{3}\times\sqrt{3}$ - R30°**	**1/3ML**	**GGA[r]**	**fcc**
Pd(111)	**p(2×2)**	**1/4ML**	**GGA[h]**	**fcc**
Re(0001)	$\sqrt{3}\times\sqrt{3}$ - R30°	1/3ML	EELS[s]	atop

[a] Ref. 44
[b] Ref. 45
[c] Ref. 46
[d] Ref. 47
[e] Ref. 48
[f] Ref. 49
[g] Ref. 50
[h] Ref. 51
[i] Ref. 52
[j] Ref. 53
[k] Ref. 54
[l] Ref. 55
[m] Ref. 56
[n] Ref. 57
[o] Ref. 58
[p] Ref. 59
[q] Ref. 60
[r] Ref. 61
[s] Ref. 62