Statistical Mechanics Improves Density Functional Theory for Electrocatalytic Metal Surface Properties and CO Binding Trends

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Abstract

Herein, we combine Density Functional Theory (DFT) with *ab initio* molecular dynamics at ambient conditions to calculate surface properties of and CO binding trends to the electrocatalytically relevant Pt(111), Cu(111), Ag(111), and Au(111) metals. By accounting for thermal effects both the RPBE GGA and the B97M-rV meta-GGA functionals show better metal surface strain trends, CO binding energetics, and the correct low-coordination site preference for the Cu(111) and Pt(111) surfaces. The importance of dispersion is evident at finite temperatures, with only B97M-rV exhibiting binding energetics in agreement with experiment for the Ag(111) and Au(111) surfaces, and is found to consist of a mixture of chemisorbed and physisorbed CO species. Overall this work begins to address a longstanding theoretical discrepancy with experimental observations on these important metals relevant to the electrochemical CO₂ reduction reaction through the full accounting of thermal fluctuations.

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INTRODUCTION

The electrochemical CO$_2$ reduction reaction (CO$_2$RR) is one of the most promising technologies available for converting greenhouse gases into useful chemicals using renewable energy sources.$^{1-3}$ Given the low concentration of CO$_2$ adsorbed at the active metal interface, the inherent mechanism of CO$_2$RR has proved to be difficult to investigate experimentally, although new spectroscopic surface sensitive and operando measurements are starting to emerge$^4$. It has also been a long–standing theoretical challenge to accurately predict the CO$_2$RR reaction mechanism by faithfully reproducing the binding energies and activation barriers observed experimentally for key species such as CO, H, OH, and COOH on electrode surfaces. CO adsorption on metal surfaces in particular has been widely treated as a benchmark for theoretical surface science studies$^5-7$, because CO is an electrocatalytically active intermediate from which viable pathways to C$_1$ and C$_2$ products are formed on Cu or known to be end products on metals such as Ag, Au, or Pt.$^5,6$

Density Functional Theory (DFT)$^8-10$ is almost universally used in catalysis modeling today$^{11}$, typically at the level of a generalized gradient approximation (GGA) due to its lower computational cost and reasonable accuracy for molecular chemistry, but has yielded mixed success for surface science and heterogeneous catalysis. A particular Achilles heel has been the inability to predict adsorption energies and adsorption-site preferences on electrocatalytically relevant metals, in which numerous theoretical studies have reported the drawbacks of the GGA functionals on predicting the physical and chemical properties of metal surfaces.$^{12-18}$ Often the most cited reasons are due to the inexact exchange–correlation term$^{19-21}$ including lack of non–local correlation which is necessary to describe dispersion interactions$^{22-24}$, and posteriori missing thermodynamic corrections$^{13,25-27}$. In response, a number of GGA functionals have been developed to better reproduce adsorption energies, such as the RPBE GGA functional which fulfills the Lieb-Oxford criterion by construction.$^{14}$

An alternative is to investigate new DFT functionals. While a number of new hybrid DFT functionals that incorporate exact-exchange and range-separation are available$^{28-31}$, they are not viable given their computational expense for the long-term goal of a complete description of the solid-liquid interface. However, one rung lower on Jacob’s ladder are the meta-GGA functionals that incur only ~4 times the expense of a GGA, and are possible contenders for a complete DFT model for electrocatalysis. Just recently a benchmark study investigating the newer meta-GGA functionals including the first-principles SCAN$^{32-34}$, semi-empirical RTPSS$^{35}$, and B97M-rV$^{36,37}$ models, reported on their ability to reproduce experimental bulk and surface relaxation properties, and CO adsorption energies and site preferences, on the M(111) where M = Pt, Cu, Ag, Au metal
surfaces in comparison to the GGA functional RPBE.\textsuperscript{38} While RPBE performed well for the benchmark bulk and surface relaxation properties, the SCAN meta-GGA\textsuperscript{32-34} and semi-empirical meta-GGA B97M-rV\textsuperscript{36,37} yielded mixed results, displaying under-relaxed surface layer displacements and/or strong overbinding of CO on Pt and Cu. Disappointingly, all DFT functionals considered did not predict the CO adsorption site preference – the atop site for all metals observed at low CO adsorbate coverage – instead predicting stronger binding to multi-coordinated metal sites. The correct binding site is a necessary prerequisite to more accurately predict the inherent mechanism of a catalytic reaction, and this has been an ongoing problem with all DFT calculations to date. But a further indicator for problems ahead for the modified RPBE functional is its inability to describe something as basic as the water dimer for which it performs very poorly.\textsuperscript{38} By contrast, the B97M–rV\textsuperscript{36,37} functional gives good performance not only on the water dimer, but also an excellent description of bulk water\textsuperscript{39,40}, revealing its potential feasibility for better theoretical predictions at the solid-liquid interface.

As is standard in nearly all electrocatalysis computational work, DFT functionals are evaluated at 0 K although all electrochemical surfaces, adsorbants, and reactions are experimentally produced under finite temperature conditions. Although thermodynamic corrections in the harmonic regime have been used, they can’t account for the genuine thermal (and pressure) fluctuations that are manifest in all catalytic experiments. Thermal energy serves as a true measure of energetic stability ($k_B T$)\textsuperscript{25,41}, and molecular fluctuations of the liquid/solid interface will undoubtedly influence the chemical pathways taken by electrochemical reactions. To address this important aspect of electrocatalysis modeling, we have used \textit{ab initio} molecular dynamics (AIMD)\textsuperscript{42,43} in the NVT and NPT ensemble to better and more directly simulate the natural statistical fluctuations of an electrocatalytic surface under ambient conditions.\textsuperscript{44}

Herein, we consider the entropic thermodynamic forces and how they manifest in the experimental bulk and surface relaxation properties, and CO adsorption energies and site preferences, on the M(111) surfaces where M = Pt, Cu, Ag, Au using the GGA functional RPBE\textsuperscript{38} and the meta-GGA functional B97M–rV\textsuperscript{36,37}. Our results show that both RPBE and B97M-rV functionals exhibit greater expansion of the top layers of the bare M(111) surface, which in turn modifies the adsorption energy and site preference of CO on all four metals. Both functionals show greatly improved binding energies for the CO binding to the Cu(111) and Pt(111) metal surfaces when evaluated at 300 K, with stronger preference for CO binding to the under-coordinated atop site for all metals at finite temperature. Thermalization exposes the importance of dispersion interactions, with only the B97M-rV functional predicting weak binding energetics in agreement with experiment for the Ag(111) and Au(111) metals evaluated here, but are seen to be a mixture
of chemisorbed and physisorbed CO species. Overall a more realistic accounting of statistical fluctuations of a canonical ensemble is shown to improve DFT agreement with experiment, setting the stage for future studies involving more realistic and robust models of the solid-liquid interface of many electrocatalytic reactions.

**RESULTS**

The model for the bulk metal and bare M(111) surfaces and adsorbate-surface sites are provided in Figure 1. Six metal layers are employed in total to describe the surface layer and bulk character of the metals, with each layer containing 36 (6 x 6) metal atoms with no constraints used to fix layers, but instead simulating periodic boundary conditions in the x-y plane. All ab initio molecular dynamics (AIMD) simulations are performed in the NVT ensemble, except for the Au(111) and Ag(111) surfaces at the RPBE level of theory which were calculated in the NPT ensemble as their NVT bulk systems were found to be unstable. Adsorption properties are averaged across nine CO molecules placed onto the surface to construct a low ~25% coverage of available metal sites, also shown in Figure 1, for which the experiments at ambient conditions indicate that the atop site is preferred for all metals examined here. All AIMD simulations reported are comprised of 2 ps trajectories, with statistics for observables collected over the last 1.5 ps. Further details are provided in Methods and in the Supplementary Information.

![Figure 1. Bulk metal and metal surface models used to describe structural relaxations and CO binding preferences.](image)

(a) The 6 x 6 model for the bare M(111) surface, with interlayer distances $d_{12}$ and $d_{23}$; the $d_{\text{bulk}}$ value is defined as the averaged distance over the last two interlayer distances. (b) Initial condition of nine adsorbed CO molecules on the surface, corresponding to a low coverage result of 0.25; only the atop site configuration is shown here, but a similar set up was used for the initial condition of the other three multi-coordinated sites (bridge, fcc, and hpc shown in Figure S1) for Pt and Cu.
Interlayer relaxation of metal surfaces.

We carried out static calculations at 0 K with the RPBE and B97M-rV functionals for the metal models displayed in Figure 1 to determine interlayer distances $d_{12}$, $d_{13}$, and $d_{23}$, values and calculated layer-layer percentage relaxations with respect to $d_{\text{bulk}}$ values for each metal at each condition. Overall, the 0 K results generated with the RPBE functional appear to agree well with the experimental data trends for Pt(111) and Cu(111), while also showing acceptable expansion trends for Au(111), but yielding poor agreement for surface relaxations for the Ag(111) metal. By contrast the interlayer distances for the B97M-rV functional at 0 K are more compressed on average across the Pt(111), Cu(111), and Au(111) metals with respect to experiment, and surface relaxation trends are also poorly reproduced for the Ag(111) metal. This result is the same for different plane wave cutoff values (Table S1) and different cell sizes and different numbers of frozen layers to better enforce the bulk lattice constant of the meta-GGA DFT model (Table S2).

Table 1. Interlayer surface relaxations for M(111) (M = Pt, Cu, Au, Ag) using RPBE and B97M-rV. All thermal calculations report NVT ensemble results, except for Au(111) and Ag(111) surfaces using RPBE which were evaluated in the NPT ensemble. The unit of distance is Å.

| Metal | RPBE | B97M-rV | Experiment |
|-------|------|---------|------------|
|       | Non-thermal | Thermal | Non-thermal | Thermal |       |
| Pt    | $d_{12}/d_{\text{bulk}}$ | +0.9% | 0.0%a | -0.9% | +0.45% | +1.6% |
|       | $d_{23}/d_{\text{bulk}}$ | +0.4% | 0.0% | -2.2% | 0.0% | 0% |
|       | $d_{13}/2d_{\text{bulk}}$ | +0.9% | +0.2% | -1.3% | +0.45% | +0.9% |
|       | $d_{\text{bulk}}$ | 2.30 | 2.33±0.03 | 2.30 | 2.27±0.02 | 2.27 |
| Cu    | $d_{12}/d_{\text{bulk}}$ | 0.0% | +0.9% | -2.5% | -0.5% | -0.7% |
|       | $d_{23}/d_{\text{bulk}}$ | -0.5% | -0.5% | +1.0% | -1.0% | -0.6% |
|       | $d_{13}/2d_{\text{bulk}}$ | -0.5% | 0.0% | -1.0% | -0.5% | -0.5% |
|       | $d_{\text{bulk}}$ | 2.09 | 2.13±0.04 | 2.09 | 2.03±0.03 | 2.09 |
| Ag    | $d_{12}/d_{\text{bulk}}$ | +2.6% | +0.9% | +1.3% | 0% | -2.5% |
|       | $d_{23}/d_{\text{bulk}}$ | +1.7% | -0.4% | -0.9% | -0.4% | +0.6% |
|       | $d_{13}/2d_{\text{bulk}}$ | +1.9% | +0.2% | 0.0% | -0.2% | -1.5% |
|       | $d_{\text{bulk}}$ | 2.34 | 2.44±0.03 | 2.34 | 2.37±0.02 | 2.36 |
| Au    | $d_{12}/d_{\text{bulk}}$ | +2.9% | +1.6% | -0.8% | +1.6% | +1.5% |
|       | $d_{23}/d_{\text{bulk}}$ | -0.4% | -0.4% | -3.9% | -0.4% | --- |
|       | $d_{13}/2d_{\text{bulk}}$ | +1.2% | +0.4% | -2.3% | +0.8% | --- |
|       | $d_{\text{bulk}}$ | 2.41 | 2.44±0.02 | 2.41 | 2.38±0.03 | 2.36 |

a The Pt(111) metal properties in the NVT ensemble are found to be the same as the NPT ensemble as tested for the RPBE functional: interlayer distances (and surface relaxations), $d_{12} = 2.34±0.02$ (+0.2%), $d_{23} = 2.34±0.03$ (+0.0%), $d_{\text{bulk}} = 2.34±0.02$, $d_{13} = 4.67±0.05$ (+0.2%), and $2d_{\text{bulk}} = 4.66±0.05$.

b Experimental data for Pt(111)45-47, Cu(111)45,48, Ag(111)47,49, and Au(111)47,50. Surface relaxations are representative for room temperature, most reporting the Debye temperature. The one exception is Au(111) which undergoes significant reconstruction and is kept colder than 300K.

But in order to better compare to the thermodynamic condition of the experiments, the surface and bulk properties evaluated with DFT should be collected as thermal averages of surface strain and
bulk metal properties, which are also provided in Table 1 and Figure 2. We note that previous experimental work has estimated a lattice heating time constant on the 1-10 ps timescale for 20 nm metal films for Cu and Au\textsuperscript{51}, which would suggest that the 2.0 ps AIMD simulation timescales (the first 0.5 ps are discarded as equilibration) are sufficient for our simulated ~1 nm thick metals.

**Figure 2. Calculated interlayer relaxation (%) of M(111) (M = Pt, Cu, Ag, Au) surfaces.** Experimental results are also depicted here for comparison. The absent error bars are all less than 0.07 Å, relative to the DFT functional dependent layer-layer distances in the bulk.

For the RPBE functional at 300 K the thermal effects weaken the M...M interactions and induce more flexibility, resulting in a larger $<d_{\text{bulk}}>$ that increase absolute error with respect to experiment (Table 1). Previous work has reported that RPBE severely underestimates cohesive energies of the four transition metals examined here\textsuperscript{52}, which likely explains the uniform expansion of the $<d_{\text{bulk}}>$ values when thermal energy is added. The thermal effect diminishes agreement with experiment for the relative surface relaxations for Pt(111) and Cu(111), although there is some improvement for Ag(111) and Au(111) (Figure 2). The ambient temperature results for the B97M–rV functional corrects the 0 K surface relaxation percentages significantly, and trends move more consistently toward the experimental data for all M(111) surfaces. For both the GGA and meta-GGA functionals, the fluctuations of the interlayer distances $<d_{13}>$ and $<2d_{\text{bulk}}>$ are generally anti-correlated (Figure S1) to maintain the stability of the whole surface, and the improvement to the $<d_{13}>$ relaxation for B97M-rV especially is attributable to its convergence to the same average
value not seen at 0 K as shown in Table 1.

**Metal surfaces with CO adsorbates**

Because the correct metal surface strain trends are attributable to the finely balanced occupation of metal $d$ states for adsorbate–surface interactions, one would conclude from Table 1 and Figure 2 that the RPBE GGA at either temperature, and the B97M-rV meta-GGA evaluated at 300 K, might be able to predict the adsorption energies and adsorbed-site preference trends for the CO intermediate, especially for the Cu(111) and Pt(111) surfaces. The popular RPBE functional in particular has provided reasonably reliable results for chemisorption energies at 0 K of relevant catalytic intermediates such as CO previously, although never the low-coordination site preference.

For Cu(111), experimental adsorption energies are available for the atop, hpc, fcc, and bridging sites, and CO site preference occurs in the order atop > fcc > hcp > bridge, whereas experimental adsorption energies for all other M(111) metals report only the atop site binding energy, as that site is thought to be strongly preferred with respect to the multi-coordinated sites. Figures 3 and 4 summarize the DFT results using the RPBE and B97M-rV functionals for CO binding energy at 0 K and CO thermodynamic surface stability at 300 K, at 25% coverage for the more strongly binding Cu(111) and Pt(111) and the weakly binding Ag(111) and Au(111) metal surfaces; numerical results are also reported in Table S3. We note that previous work for CO on Cu found that timescales for phonon coupling is on the ~ 1 ps timescale, and thus our AIMD simulation timescales are sufficient for establishing at least CO binding trends. Here we emphasize a few general observations as well as a number of surprises that emerge from the comparison of the DFT functionals under the different thermodynamic conditions for CO adsorption energetics and metal site preferences on the M(111) surfaces.

Both DFT functionals improve their agreement with experiment for the CO chemisorption energies for Cu(111) and Pt(111), in which thermalization corrects for the overbinding at 0 K (Figure 3a and 3b), and in which both prefer the atop site as well. However, with thermalization the RPBE functional now slightly underbinds CO to Cu(111) on average, and does not predict the experimental chemisorption energy trend for the other sites. By contrast the meta-GGA functional at 300 K predicts the relative binding energy trend with coordination site consistent with experiment, and correctly ranks the bridge site as least stable for Cu(111) as is evident in the dynamics (Figure 3c). The quantitative results can be quite sensitive to the pseudopotential as we have shown previously, and the plane wave cutoff plays a role too (Figure S2), but the qualitative effect of thermal fluctuations is to create slightly larger M–C–O angles and longer M–C distances as the main indicator of a weakened bonding interaction between the metal at the
atop site and the adsorbed CO (Figure 3d and Table S4).

Figure 3. Thermal effect on adsorption energies for CO on M(111) surfaces for 25% coverage reported by experiment. Calculated and experimentally observed adsorption energies for CO on the atop, bridge, fcc and hcp sites at 0 and 300 K for (a) Cu(111) and (b) Pt(111). All numerical values are provided in Table S3. We used time-averaged energies for each system to calculate the adsorption energies as explained in the Method section. We note that even at 0 K we find that the RPBE functional prefers the atop site, although this is dependent on cutoff values (Figure S2); calculations using 400 Ry and 1200 Ry cutoff values prefer the atop site at 0 K, but the fcc site is the most preferred at 800 Ry cutoff. Absent error bars are all less than 0.02 eV/CO. (c) Binding energy vs. time for B97M-rV, illustrating CO adsorbed on Cu(111) surface at the bridge site for the first 100 fs, but moving to the atop position due to the strong energetic preference for CO binding at this site. (d) Representative geometries from two different perspectives of the CO adsorbed on Cu(111) at the atop site for both B97M-rV and RPBE, showing the deviations from linearity of the M-C=O angle at 300 K.

For Pt(111) we used a small core pseudopotential for the DFT functionals which we have shown previously results in small errors when benchmarked on a single metal-carbonyl system using a high quality hybrid DFT functional.\textsuperscript{38,64} In this case the CO binding energy at the atop site of the metal with RPBE using AIMD are in good numerical agreement with experiment, but there is a stronger preference for the CO to bind at the hcp site at 0 K and 300 K. Although the CO binding energy for Pt(111) is still overbound by ~0.2 eV/CO using B97M-rV at 300 K, it prefers the atop site in agreement with experiment. On the basis of radial distribution function $g_{M-C}(r)$ generated, the integration under the first peak indicates that there is 100% chemisorbed CO at any temperature for both DFT functionals (Figure S3).
Figure 4. Thermal effects on CO binding to the weakly binding Ag(111) and Au(111) surfaces. Shown are the radial distribution function (RDF) between the metal and carbon of CO, \( g_{M-C}(r) \), for RPBE and B97M–\( rV \) after 1.5 ps (black) and 2.0 ps (red) of AIMD production runs, and the corresponding integration to assess the running coordination number across the 9 atop sites on the surface. The blue dash lines correspond to the chemical adsorption and the region between blue and black dash lines present the physical adsorption; beyond the RDFs are probing second nearest neighbors. Representative snapshots are depicted to show the mixture of chemisorbed, physisorbed, and/or desorbed CO molecules (circled in green) at the last 1.5 ps time point of the AIMD simulation. The statistical data is collected after 500 fs’s pre-equilibration for the 2 ps trajectories. (a) \( g_{Ag-C}(r) \) and (b) \( g_{Au-C}(r) \) and running coordination for RPBE at different time scales showing continual loss of CO and preferences for the gas phase. (c) \( g_{Ag-C}(r) \) and (d) \( g_{Au-C}(r) \) and running coordination for B97M–\( rV \) showing a mixture of chemisorbed and physisorbed CO.
The same calculations were performed for the CO adsorption energy on the atop site of the Ag(111) and Au(111) metal surfaces (Figure 4). For the RPBE functional at either temperature, CO is predicted to be more stable in the gas phase for the two weaker binding metal surfaces, given their positive adsorption energies (Table S3). According to Figure 4a and 4b, the first $g_{M-C}(r)$ peak gradually shrinks in the simulations over time, indicating that the number of initially bound CO molecules on Au(111) and Ag(111) surfaces is decreasing, and for which we observe the near complete dissociation of CO from Ag(111) on the 2 ps timescale of the AIMD simulation. The observation that CO effectively does not bind to the weak metal surfaces using the RPBE functional, with or without thermalization, arises in part from the lack of a dispersion interaction term, unlike the B97M-rV functional.

In fact the B97M-rV functional exhibits binding energetics that agree with experiment on the atop site at any temperature, with better agreement found for Ag(111) than for Au(111). More interestingly, the thermalized weak binding surfaces reveal a mixture of chemisorbed and physisorbed CO molecules for the B97M-rV functional, with ~6 CO (~64%) and ~7 CO (~80%) molecules chemisorbed on Ag(111) and Au(111) surface, respectively, with the remaining CO’s located up to ~4.0 Å from the adsorption site, which would be the evidence for physisorption. But given the good agreement with experiment for the free energy of CO binding to the Au(111) and Ag(111) surfaces, the B97M-rV result would propose that experiments might be measuring a mixture of chemisorbed and physisorbed CO species. Thermal fluctuations create much larger M–C–O angles and longer M–C distances for the chemisorbed species at the atop site on the Au(111) and Ag(111) surfaces which would diminish the binding strength further compared to the stronger binding Pt(111) and Cu(111) metals (Table S4).

**DISCUSSION AND CONCLUSION**

In this work we have eschewed post-calculation (harmonic) thermodynamic corrections in favor of ab initio molecular dynamics that directly accounts for thermal fluctuations of the M(111) surfaces M=[Ag, Au, Cu, and Pt] and their CO binding motifs. We have compared two different DFT functionals, the GGA RPBE and the meta-GGA B97M-rV, which were chosen for several reasons. First and foremost they are computationally affordable when one looks ahead to the next goal of atomistic modeling of the solid-liquid interface. Second the RPBE functional has become a popular choice for surface science studies and electrocatalysis applications, whereas meta-GGAs such as the B97M-rV functional is still undergoing evaluation across a range of applications. Finally, we believe that several general conclusions can be drawn in regards
the effect of the entropic effects for DFT by considering these two functionals specifically.

Previous work has reported that the overall performance of RPBE for lattice parameters, cohesive energies, and surface energies of the four transition metals examined here is worse than that of the parent PBE functional\textsuperscript{52}, in spite of its better performance for describing chemisorption energies for molecules like CO. This would suggest that RPBE at 0 K has a reliance on the severe underestimation of cohesive metal energies\textsuperscript{52}, to create reasonable metal configurations to enable good CO binding trends across a range of metals. But we find that all of the metals systematically expand when RPBE is simulated at 300 K, which is manifest in some slight underbinding and inconsistent site preferences for CO binding on Cu(111), and complete CO desorption on the Ag(111) and Au(111) surfaces even given the short length of our (painfully collected) AIMD simulations, a result consistent with its lack of any dispersion model.

The metal surface contractions evaluated with the B97M-rV functional evaluated at 0 K are greater than RPBE and experiment, and thus thermal energy flow systematically expands the metal surfaces too, but now in such a way to describe more correctly all interlayer distances and surface relaxation properties of the four metals. Consistent with these findings, the B97M-rV functional systematically prefers the atop adsorption site for CO for the Cu(111) and Pt(111) surfaces, reproduces the relative binding energy trends for the remaining multi-coordinated sites for Cu(111), and CO is found to weakly bind to the atop adsorption site for Ag(111) and Au(111) surfaces with energetics in remarkable agreement with the experimental observations. Although the AIMD simulations used here are quite short, we expect the following qualitative results to hold with B97M-rV, namely, that while the Pt(111) and Cu(111) surfaces show complete chemisorption of CO, the experiments may actually be reporting an average of chemisorbed and a small fraction of physisorbed species on the Ag(111) and Au(111) surfaces. Furthermore, because the B97M-rV meta-GGA gives an excellent description of bulk water properties\textsuperscript{39,40}, and combined with this work better establishes a theoretical foundation for describing the electrolyte properties at the electrocatalytic surface in the future.

Finally, we believe a few general trends learned in this work on RPBE and B97M-rV in particular will hold when evaluating any DFT functional in general. Thermal effects are seen to populate different normal modes of the metal surface, causing a significant change in their surface relaxation profiles. Because these surface strain trends correlate with CO binding motifs, thermalized statistical averaging influences the preferred CO adsorption site and the relative strength of binding to other sites on any given metal surface. Although predicting the CO absorption preference on the atop site of electrocatalytic metals has eluded DFT previously, we suspect that DFT functionals which are more accurate for intermolecular interactions, when
properly evaluated at ambient conditions, will on average determine this site preference correctly
more often than not.

In summary, the continued quest to find reliable theory to understand mechanisms for
CO2RR (and other coupled reactions such as the oxygen evolution reaction) has traditionally
focused on better quantum mechanics but less so on the statistical mechanics that is required to
match the laboratory conditions for electrocatalysis. In this work we have shown that these oft
separated theoretical frameworks ignores the true nature of statistical fluctuations on top of what
may or may not be a reasonable potential energy surface with a given level of quantum mechanics.
That is, the relative performance of any DFT functional at 0 K for describing interlayer relaxations
and CO adsorption energies at 300 K is not always reliable – and a more meaningful comparison
is the ability to describe an experiment at or near the thermodynamic state point at which data is
collected. At the same time, a better study on the relative merits of DFT for describing
electrocatalysis must go beyond this work, as there are still unresolved issues around simulation
time scales, pseudopotentials, basis sets, distance cutoffs, numerical quadrature, and differences
in software packages. Nonetheless our results suggest that DFT functionals might be better than
we thought for electrocatalysis, or at least not as bad as we feared, upon full consideration of the
detailed fluctuations of a complete statistical mechanical ensemble.

**METHODS**

All calculations were carried out with DFT using the dispersion corrected meta-GGA functional
B97M–rV\(^{36,37}\) and revised GGA RPBE\(^{14}\) method in combination with TZVP basis sets optimized
for multigrid integration\(^{66}\) as implemented in the CP2K package\(^{67,68}\). The normal-conserving
pseudopotentials\(^{69}\) were used for describing the interactions between the frozen cores and electrons
in valence shells. In all cases, we used periodic boundary conditions with a cutoff value of 400 Ry
and relative cutoff of 60 Ry. All the slabs were repeated periodically with a 15 Å vacuum layer
between the images in the direction of the surface normal.

**Static 0 K calculations.** Based on previous work we established a bulk model within the GPW
formalism, by replicating the unit cell four times along the three cell axes (264 atoms in total).\(^{38}\)
Using the parameters obtained from bulk calculations, the slab model was built with a different
number of surface layers for testing. Results presented in the main text are for the case of a 6 × 6
× 6 supercell with three bottom layers frozen. For the CO adsorbed systems at a coverage of \(~\)0.25,
nine CO molecules were put onto the surface at equal spacing. During the geometry optimizations,
the converged criteria were \(3 \times 10^{-3}\) bohr for atomic displacements and \(4.5 \times 10^{-4}\) hartree/bohr for
the forces.

**AIMD simulations at 300 K.** We investigated thermal effects by using AIMD simulations, with a slab model containing six layers with $6 \times 6$ atoms per layer; no layers were fixed in the simulations. All molecular dynamics simulations with the B97M–rV functional are performed by sampling in the canonical (NVT) ensemble employing Nose–Hoover thermostats$^{70,71}$, with a time step of 1 fs and a temperature of 300 K. The same NVT protocol was used for the RPBE functional for Pt(111) and Cu(111), but the NVT simulations led to large distortions of the structure for Ag(111) and Au(111) metals. Hence for the latter we then used an isobaric-isothermal ensemble (NPT)$^{72}$ for these two surfaces. Statistical averages were collected over 2 ps of production after 0.5 ps equilibration, where convergence was measured by the settling of the energy fluctuation to $\sim 0.25$ kcal mol$^{-1}$ per atom. Using the equilibrated structure, we add CO adsorbates onto different sites of the surface according to the geometries obtained in the static calculations, and ran an additional 1.5 ps starting from 15 independent equilibrated trajectories of the surface calculations. The time-averaged distances and adsorption energies are generated from all the trajectories during equilibration. Herein, the time-averaged adsorption energy is calculated as:

$$<\Delta E_{\text{ads}}>_{300K} = [<E(M-9CO)>_{300K} - 9<E(CO)>_{300K} - <E(M)>_{300K}]/9$$

And to quantify the error of the statistical values, we consider the standard deviation based on the distance and energy fluctuations:

$$\sigma = \sqrt{\frac{1}{N} \sum_{i}^{N} (\bar{X}_i - \langle \bar{X}_i \rangle)^2}$$

The time-averaged $\bar{X}_i$ value is collected on each 100 fs.

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**Conflict of interest.** The authors declare that they have no conflict of interest.

**Author contribution.** T.H-G. conceived the research, W.-L. L., V. W. and C. L. performed the calculations, and W.-L. L. created the Figures and the Table of Contents image. W.-L. L. and T.H-G. wrote the manuscript. W.-L. L., C. L., V. W., E. R., M. H-G., A.T.B., and T.H-G. contributed insights and edited the manuscript together.
Data availability. The data that supports the findings of this study are available from the corresponding author upon request.

REFERENCES

1. Hoshi, N., Kato, M. & Hori, Y. Electrochemical reduction of CO2 on single crystal electrodes of silver Ag(111), Ag(100) and Ag(110). *Journal of Electroanalytical Chemistry* **440**, 283-286, doi:https://doi.org/10.1016/S0022-0728(97)00447-6 (1997).

2. Durand, W. J., Peterson, A. A., Studt, F., Abild-Pedersen, F. & Nørskov, J. K. Structure effects on the energetics of the electrochemical reduction of CO2 by copper surfaces. *Surface Science* **605**, 1354-1359, doi:https://doi.org/10.1016/j.susc.2011.04.028 (2011).

3. Lu, Q. et al. A selective and efficient electrocatalyst for carbon dioxide reduction. *Nature Communications* **5**, 3242, doi:10.1038/ncomms4242 (2014).

4. Handoko, A. D., Wei, F., Jenndy, Yeo, B. S. & Seh, Z. W. Understanding heterogeneous electrocatalytic carbon dioxide reduction through operando techniques. *Nature Catalysis* **1**, 922-934, doi:10.1038/s41929-018-0182-6 (2018).

5. Qiao, J., Liu, Y., Hong, F. & Zhang, J. A review of catalysts for theelectroreduction of carbon dioxide to produce low-carbon fuels. *Chemical Society Reviews* **43**, 631-675, doi:10.1039/C3CS60323G (2014).

6. Jovanov, Z. P. et al. Opportunities and challenges in the electrocatalysis of CO2 and CO reduction using bifunctional surfaces: A theoretical and experimental study of Au–Cd alloys. *Journal of Catalysis* **343**, 215-231, doi:https://doi.org/10.1016/j.jcat.2016.04.008 (2016).

7. Sun, J., Marsman, M., Ruzsinszky, A., Kresse, G. & Perdew, J. P. Improved lattice constants, surface energies, and CO desorption energies from a semilocal density functional. *Physical Review B* **83**, 121410, doi:10.1103/PhysRevB.83.121410 (2011).

8. Hohenberg, P. & Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **136**, B864-B864 (1964).

9. Kohn, W. & Sham, L. Self-consistent equations including exchange and correlation effects. *Phys. Rev.* **140**, A1133-A1138 (1965).

10. Kohn, W., Becke, A. D. & Parr, R. G. Density functional theory of electronic structure. *J. Phys. Chem.* **100**, 12974-12980 (1996).

11. Bell, A. T. & Head-Gordon, M. Quantum Mechanical Modeling of Catalytic Processes. *Annu. Rev. Chem. Biomol. Eng.* **2**, 453-477 (2011).

12. Mallikarjun Sharada, S., Bligaard, T., Luntz, A. C., Kroes, G.-J. & Nørskov, J. K. SBH10: A Benchmark Database of Barrier Heights on Transition Metal Surfaces. *The Journal of Physical Chemistry C* **121**, 19807-19815, doi:10.1021/acs.jpcc.7b05677 (2017).

13. Schimka, L. et al. Accurate surface and adsorption energies from many-body perturbation theory. *Nature Materials* **9**, 741-744, doi:10.1038/nmat2806 (2010).

14. Hammer, B., Hansen, L. B. & Nørskov, J. K. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Physical Review B* **59**, 7413-7421, doi:10.1103/PhysRevB.59.7413 (1999).
15 Feibelman, P. J. et al. The CO/Pt(111) Puzzle. *The Journal of Physical Chemistry B* **105**, 4018-4025, doi:10.1021/jp002302t (2001).

16 Wellendorff, J. et al. A benchmark database for adsorption bond energies to transition metal surfaces and comparison to selected DFT functionals. *Surface Science* **640**, 36-44, doi:https://doi.org/10.1016/j.susc.2015.03.023 (2015).

17 Zhao, Q. & Kulik, H. J. Stable Surfaces That Bind Too Tightly: Can Range-Separated Hybrids or DFT+U Improve Paradoxical Descriptions of Surface Chemistry? *The Journal of Physical Chemistry Letters* **10**, 5090-5098, doi:10.1021/acs.jpclett.9b01650 (2019).

18 Stroppa, A. & Kresse, G. The shortcomings of semi-local and hybrid functionals: what we can learn from surface science studies. *New Journal of Physics* **10**, 063020, doi:10.1088/1367-2630/10/6/063020 (2008).

19 Cohen, A. J., Mori-Sánchez, P. & Yang, W. Insights into Current Limitations of Density Functional Theory. *Science* **321**, 792-794, doi:10.1126/science.1158722 (2008).

20 Cohen, A. J., Mori-Sánchez, P. & Yang, W. Fractional spins and static correlation error in density functional theory. *The Journal of Chemical Physics* **129**, 121104, doi:10.1063/1.2987202 (2008).

21 Cohen, A. J., Mori-Sánchez, P. & Yang, W. Challenges for Density Functional Theory. *Chemical Reviews* **112**, 289-320, doi:10.1021/cr200107z (2012).

22 Grimme, S. Seemingly Simple Stereoelectronic Effects in Alkane Isomers and the Implications for Kohn–Sham Density Functional Theory. *Angewandte Chemie International Edition* **45**, 4460-4464, doi:10.1002/anie.200604448 (2006).

23 Černý, J. & Hobza, P. Non-covalent interactions in biomacromolecules. *Physical Chemistry Chemical Physics* **9**, 5291-5303, doi:10.1039/B704781A (2007).

24 Vydrov, O. A. & Van Voorhis, T. Nonlocal van der Waals Density Functional Made Simple. *Physical Review Letters* **103**, 063004, doi:10.1103/PhysRevLett.103.063004 (2009).

25 Wang, Y., Babin, V., Bowman, J. M. & Paesani, F. The Water Hexamer: Cage, Prism, or Both. Full Dimensional Quantum Simulations Say Both. *Journal of the American Chemical Society* **134**, 11116-11119, doi:10.1021/ja304528m (2012).

26 Carrasco, J., Hodgson, A. & Michaelides, A. A molecular perspective of water at metal interfaces. *Nature Materials* **11**, 667-674, doi:10.1038/nmat3354 (2012).

27 Duan, S., Zhang, I. Y., Xie, Z. & Xu, X. Identification of Water Hexamer on Cu(111) Surfaces. *Journal of the American Chemical Society* **142**, 6902-6906, doi:10.1021/jacs.0c01549 (2020).

28 Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **98**, 5648-5652 (1993).

29 Yu, H. S., He, X., Li, S. L. & Truhlar, D. G. MN15: A Kohn-Sham global-hybrid exchange-correlation density functional with broad accuracy for multi-reference and single-reference systems and noncovalent interactions. *CHEMICAL SCIENCE* **7**, 5032-5051 (2016).

30 Zhao, Y. & Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **120**, 215-241 (2008).

31 Chai, J.-D. & Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.* **10**, 6615-6620 (2008).
32 Sun, J. et al. Semilocal and hybrid meta-generalized gradient approximations based on the understanding of the kinetic-energy-density dependence. *J. Chem. Phys.* **138**, 044113-044113 (2013).
33 Sun, J. et al. Accurate first-principles structures and energies of diversely bonded systems from an efficient density functional. *Nature Chem.* **8**, 831-836 (2016).
34 Sun, J., Ruzsinszky, A. & Perdew, J. P. Strongly Constrained and Appropriately Normed Semilocal Density Functional. *Phys. Rev. Lett.* **115**, 036402-036402 (2015).
35 Garza, A. J., Bell, A. T. & Head-Gordon, M. Nonempirical Meta-Generalized Gradient Approximations for Modeling Chemisorption at Metal Surfaces. *Journal of Chemical Theory and Computation* **14**, 3083-3090, doi:10.1021/acs.jctc.8b00288 (2018).
36 Mardirossian, N. et al. Use of the rVV10 Nonlocal Correlation Functional in the B97M-V Density Functional: Defining B97M-rV and Related Functionals. *The Journal of Physical Chemistry Letters* **8**, 35-40, doi:10.1021/acs.jpclett.6b02527 (2017).
37 Mardirossian, N. & Head-Gordon, M. Mapping the genome of meta-generalized gradient approximation density functionals: The search for B97M-V. *The Journal of Chemical Physics* **142**, 074111, doi:10.1063/1.4907719 (2015).
38 Lininger, C. N. et al. Challenges for DFT: Calculation of CO Adsorption on Electrocatalytically Relevant Metals. *submitted* (2020).
39 Ruiz Pestana, L., Mardirossian, N., Head-Gordon, M. & Head-Gordon, T. Ab initio molecular dynamics simulations of liquid water using high quality meta-GGA functionals. *Chemical Science* **8**, 3554-3565, doi:10.1039/C6SC04711D (2017).
40 Ruiz Pestana, L., Marsalek, O., Markland, T. E. & Head-Gordon, T. The Quest for Accurate Liquid Water Properties from First Principles. *J Phys Chem Lett* **9**, 5009-5016, doi:10.1021/acs.jpclett.8b02400 (2018).
41 Michaelides, A. & Morgenstern, K. Ice nanoclusters at hydrophobic metal surfaces. *Nature Materials* **6**, 597-601, doi:10.1038/nmat1940 (2007).
42 Car, R. & Parrinello, M. Unified Approach for Molecular Dynamics and Density-Functional Theory. *Physical Review Letters* **55**, 2471-2474, doi:10.1103/PhysRevLett.55.2471 (1985).
43 Tuckerman, M. E. Ab initiomolecular dynamics: basic concepts, current trends and novel applications. *Journal of Physics: Condensed Matter* **14**, R1297-R1355, doi:10.1088/0953-8984/14/50/202 (2002).
44 Vaissier Welborn, V. & Head-Gordon, T. Computational Design of Synthetic Enzymes. *Chemical Reviews*, doi:10.1021/acs.chemrev.8b00399 (2018).
45 Materer, N. et al. Dynamical LEED analyses of the Pt(111)-p(2×2)-NO and the Ni(111)-c(4×2)-2NO structures: substrate relaxation and unexpected hollow-site adsorption. *Surface Science* **303**, 319-332, doi:https://doi.org/10.1016/0039-6028(94)90779-X (1994).
46 Krupski, K., Moors, M., Jóźwik, P., Kobiela, T. & Krupski, A. Structure Determination of Au on Pt(111) Surface: LEED, STM and DFT Study. *Materials* **8**, 2935-2952 (2015).
47 Wan, J., Fan, Y. L., Gong, D. W., Shen, S. G. & Fan, X. Q. Surface relaxation and stress of fcc metals: Cu, Ag, Au, Ni, Pd, Pt, Al and Pb. *Modelling and Simulation in Materials Science and Engineering* **7**, 189-206, doi:10.1088/0965-0393/7/2/005 (1999).
48 Lindgren, S. Å., Waldén, L., Rundgren, J. & Westrin, P. Low-energy electron diffraction from Cu(111): Subthreshold effect and energy-dependent inner potential; surface relaxation and metric distances between spectra.
49 Statiris, P., Lu, H. C. & Gustafsson, T. Temperature dependent sign reversal of the surface contraction of Ag(111). *Physical Review Letters* **72**, 3574-3577, doi:10.1103/PhysRevLett.72.3574 (1994).

50 Nichols, R. J., Nouar, T., Lucas, C. A., Haiss, W. & Hofer, W. A. Surface relaxation and surface stress of Au(111). *Surface Science* **513**, 263-271, doi: [https://doi.org/10.1016/S0039-6028(02)01510-8](https://doi.org/10.1016/S0039-6028(02)01510-8) (2002).

51 Ligges, M. *et al*. Observation of ultrafast lattice heating using time resolved electron diffraction. *Applied Physics Letters* **94**, 101910, doi:10.1063/1.3095497 (2009).

52 Janthon, P., Kozlov, S. M., Viñes, F., Limtrakul, J. & Illas, F. Establishing the Accuracy of Broadly Used Density Functionals in Describing Bulk Properties of Transition Metals. *Journal of Chemical Theory and Computation* **9**, 1631-1640, doi:10.1021/ct3010326 (2013).

53 Mavrikakis, M., Hammer, B. & Nørskov, J. K. Effect of Strain on the Reactivity of Metal Surfaces. *Physical Review Letters* **81**, 2819-2822, doi:10.1103/PhysRevLett.81.2819 (1998).

54 Hinch, B. J. & Dubois, L. H. First-order corrections in modulated molecular beam desorption experiments. *Chemical Physics Letters* **171**, 131-135, doi: [https://doi.org/10.1016/0009-2614(90)80063-J](https://doi.org/10.1016/0009-2614(90)80063-J) (1990).

55 Hollins, P. & Pritchard, J. Interactions of CO molecules adsorbed on Cu(111). *Surface Science* **89**, 486-495, doi: [https://doi.org/10.1016/0039-6028(79)90633-2](https://doi.org/10.1016/0039-6028(79)90633-2) (1979).

56 Brown, W. A., Kose, R. & King, D. A. Femtomole Adsorption Calorimetry on Single-Crystal Surfaces. *Chemical Reviews* **98**, 797-832, doi:10.1021/cr9700890 (1998).

57 Fischer-Wolfarth, J.-H. *et al*. An improved single crystal adsorption calorimeter for determining gas adsorption and reaction energies on complex model catalysts. *Review of Scientific Instruments* **82**, 024102, doi:10.1063/1.3544020 (2011).

58 Schießer, A., Hörtz, P. & Schäfer, R. Thermodynamics and kinetics of CO and benzene adsorption on Pt(111) studied with pulsed molecular beams and microcalorimetry. *Surface Science* **604**, 2098-2105, doi: [https://doi.org/10.1016/j.susc.2010.09.001](https://doi.org/10.1016/j.susc.2010.09.001) (2010).

59 Campbell, C. T., Ertl, G., Kuipers, H. & Segner, J. A molecular beam investigation of the interactions of CO with a Pt(111) surface. *Surface Science* **107**, 207-219, doi: [https://doi.org/10.1016/0039-6028(81)90621-X](https://doi.org/10.1016/0039-6028(81)90621-X) (1981).

60 Kelemen, S. R., Fischer, T. E. & Schwarz, J. A. The binding energy of CO on clean and sulfur covered platinum surfaces. *Surface Science* **81**, 440-450, doi: [https://doi.org/10.1016/0039-6028(79)90111-0](https://doi.org/10.1016/0039-6028(79)90111-0) (1979).

61 McElhinney, G., Papp, H. & Pritchard, J. The adsorption of Xe and CO on Ag(111). *Surface Science* **54**, 617-634, doi: [https://doi.org/10.1016/0039-6028(76)90209-0](https://doi.org/10.1016/0039-6028(76)90209-0) (1976).

62 Gajdo, M., Eichler, A. & Hafner, J. CO adsorption on close-packed transition and noble metal surfaces: trends from ab initio calculations. *Journal of Physics: Condensed Matter* **16**, 1141-1164, doi:10.1088/0953-8984/16/8/001 (2004).

63 Springer, C., Head-Gordon, M. & Tully, J. C. Simulations of femtosecond laser-induced desorption of CO from Cu(100). *Surface Science* **320**, L57-L62, doi: [https://doi.org/10.1016/0039-6028(94)00569-9](https://doi.org/10.1016/0039-6028(94)00569-9) (1994).

64 Rossomme, E., Lininger, C. N., Bell, A. T., Head-Gordon, T. & Head-Gordon, M. Electronic structure calculations permit identification of the driving forces behind frequency shifts in transition metal monocarboxyls. *Physical Chemistry Chemical Physics* **22**, 781-798, doi:10.1039/C9CP04643G (2020).

65 Welborn, V. V., Li, W.-L. & Head-Gordon, T. Interplay of water and a supramolecular capsule for catalysis of reductive elimination reaction from gold. *Nature Communications* **11**, 415, doi:10.1038/s41467-019-14251-6
66 VandeVondele, J. & Hutter, J. Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. *The Journal of Chemical Physics* **127**, 114105, doi:10.1063/1.2770708 (2007).
67 Hutter, J., Iannuzzi, M., Schiffmann, F. & VandeVondele, J. cp2k: atomistic simulations of condensed matter systems. *WIREs Computational Molecular Science* **4**, 15-25, doi:10.1002/wcms.1159 (2014).
68 VandeVondele, J. *et al.* Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Computer Physics Communications* **167**, 103-128, doi:https://doi.org/10.1016/j.cpc.2004.12.014 (2005).
69 Goedecker, S., Teter, M. & Hutter, J. Separable dual-space Gaussian pseudopotentials. *Physical Review B* **54**, 1703-1710, doi:10.1103/PhysRevB.54.1703 (1996).
70 Nosé, S. A unified formulation of the constant temperature molecular dynamics methods. *The Journal of Chemical Physics* **81**, 511-519, doi:10.1063/1.447334 (1984).
71 Hoover, W. G. Canonical dynamics: Equilibrium phase-space distributions. *Physical Review A* **31**, 1695-1697, doi:10.1103/PhysRevA.31.1695 (1985).
72 Evans, D. J. & Morriss, G. P. The isothermal/isobaric molecular dynamics ensemble. *Physics Letters A* **98**, 433-436, doi:https://doi.org/10.1016/0375-9601(83)90256-6 (1983).