

First-principles extrapolation method for accurate CO adsorption energies on metal surfaces

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We show that a simple first-principles correction based on the difference between the singlet-triplet CO excitation energy values obtained by density-functional theory (DFT) and high-level quantum chemistry methods yields accurate CO adsorption properties on a variety of metal surfaces. We demonstrate a linear relationship between the CO adsorption energy and the CO singlet-triplet splitting, similar to the linear dependence of CO adsorption energy on the energy of the CO $2\pi^*$ orbital found recently [Kresse *et al.*, Phys. Rev. B **68**, 073401 (2003)]. Converged DFT calculations underestimate the CO singlet-triplet excitation energy ΔE_{S-T} , whereas coupled-cluster and configuration-interaction (CI) calculations reproduce the experimental ΔE_{S-T} . The dependence of E_{chem} on ΔE_{S-T} is used to extrapolate E_{chem} for the top, bridge, and hollow sites for the (100) and (111) surfaces of Pt, Rh, Pd, and Cu to the values that correspond to the coupled cluster and CI ΔE_{S-T} value. The correction reproduces experimental adsorption site preference for all cases and obtains E_{chem} in excellent agreement with experimental results.

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I. INTRODUCTION

The chemisorption of carbon monoxide on transition metal surfaces is regarded as a prototypical system for the study of molecule-surface interactions and has been intensely studied theoretically and experimentally.¹ For first-principles theoretical studies, density-functional theory (DFT) with the generalized gradient approximation (GGA) for the exchange-correlation functional has emerged as the method of choice, and DFT-GGA studies have significantly advanced understanding of surface phenomena.^{2,3}

Despite these successes, two of the most basic properties of CO-metal surface interactions—the chemisorption energy and the preferred adsorption site—cannot be reliably predicted by DFT calculations. Theoretical CO chemisorption energies obtained by the widely used PW91 (Ref. 4) and PBE (Ref. 5) functionals are significantly higher than experimental values, sometimes by as much as 0.4 eV (Ref. 6) (30%). The RPBE functional⁶ does improve the adsorption energetics, but at the expense of lower accuracy in metal lattice constants and a severe underestimation of surface energies. Even more importantly, neither PBE nor RPBE calculations can correctly predict the relative energetics of the high symmetry sites, favoring the more coordinated bridge and hollow sites over the top site, and resulting in a wrong site preference in a number of systems. This was first discussed by Feibelman *et al.*⁷ where a variety of DFT-GGA methodologies and codes predicted adsorption at the fcc or hcp hollow site to be preferred over the experimentally preferred top site adsorption on the Pt(111) surface at low coverage. Since then this “puzzle” has been addressed^{8–11} and the DFT-GGA inaccuracy traced to the incorrect description of CO electronic structure and bond breaking.

Grinberg *et al.* showed that the inaccuracy in site preference was due to the poor treatment of CO bond breaking by GGA functionals. Analyzing the CO electronic structure, Gil *et al.* found that PBE and B3LYP (Refs. 12,13) functionals

place the unfilled CO $2\pi^*$ orbital too low in energy. This makes it too close in energy to the metal d band, which results in an unrealistic strengthening of the $2\pi^*$ - d -band bonding interaction. More recently, Kresse and co-workers¹¹ used DFT calculations of varying accuracy and showed that a linear relationship exists between the difference of top and hollow site chemisorption energies for CO on Pt(111) and the gas-phase energy of the CO $2\pi^*$ orbital.

By using a GGA + U type functional, Kresse *et al.*¹¹ were able to adjust the energetic position of the gas-phase CO $2\pi^*$ orbital, restoring the correct prediction that top site adsorption is preferred on Pt(111). However, the “correct” value of U is not known *a priori*. Furthermore, they studied adsorption on Pt(111) and did not address CO on other metal surfaces. In this paper, we demonstrate that a linear relationship exists between the CO chemisorption energy and the CO singlet-triplet excitation energy for the top, bridge, and hollow sites on a variety of metal surfaces. Unlike the energetic position of the $2\pi^*$ orbital, the CO singlet-triplet excitation energy is rigorously well defined and is accurately computed by coupled-cluster¹⁴ and configuration-interaction (CI) quantum chemical calculations.¹⁵ Extrapolation of E_{chem} values to the correct CO singlet-triplet excitation energy relies only on first-principles calculations, and yields chemisorption and site-preference energies in excellent agreement with experiment for all systems studied.

II. METHODOLOGY

Calculations are carried out using the PBE GGA exchange-correlation functional⁵ and norm-conserving optimized pseudopotentials¹⁶ with the designed nonlocal method¹⁷ for metals. All pseudopotentials were constructed using the OPIUM pseudopotential package.¹⁸ CO chemisorption is modeled at 1/4 monolayer coverage on five layer slabs, separated by vacuum, with relaxation allowed in the top two layers. All calculations are done, and tested to be

TABLE I. Pseudopotential details. Core radii are in a_0 , plane-wave cutoffs q_c in Ry. All PSPs were created from the s^2p^2 reference configuration for carbon and the s^2p^4 reference configuration for oxygen. For each pseudopotential set, results from gas-phase molecule calculations for the $2\pi^*$ energy, as well as the $5\sigma-2\pi^*$ gap and the singlet-triplet energy are given, all in eV.

	r_c^O, r_c^C	q_c^O, q_c^C	$E_{2\pi^*}$	$5\sigma-2\pi^*$	ΔE_{S-T}
PSP 1	0.94,1.09	81,81	-2.10	6.91	5.35
PSP 2	1.60,1.49	47,50	-1.90	7.01	5.53
PSP 3	1.70,1.49	30,50	-1.61	7.35	5.84
PSP 4	1.65,1.49	42,50	-1.94	7.04	5.56
PSP 5	1.70,1.49	39,50	-1.87	7.09	5.61

converged, using a $4 \times 4 \times 1$ grid of Monkhorst-Pack k -points.¹⁹ The Kohn-Sham orbitals are expanded in a plane-wave basis set truncated at either 81 or 50 Ry, the higher cutoff being required in calculations using C and O pseudopotentials with small real-space cutoffs. We calculate the chemisorption energy for CO adsorbed on the (111) and (100) surfaces of Pt, Rh, Pd, and Cu, in three high-symmetry sites: top, bridge, and hollow. On the (111) surfaces, adsorption at the fcc hollow site is not reported, since it is well known that differences between calculated fcc and hcp hollow site adsorption energies are negligible.^{20,21}

We repeat these calculations using different sets of C and O pseudopotentials described in Table I. We use three sets of C and O pseudopotentials to calculate E_{chem} at each site on each surface. To evaluate whether three data points are adequate to describe trends in the chemisorption energies, we expand the number of C and O pseudopotential sets to five, and repeat the calculations for the hollow site on Pt(111). The slope for $E_{\text{chem}}^{\text{GGA}}$ versus ΔE_{S-T} is unchanged on going from three points to five, as is the goodness of fit. Based on this, the remainder of our results use the first three pseudopotential sets.

III. RESULTS

For CO on Pt(111), our calculations show a linear relationship between $E_{\text{chem}}^{\text{hcp}}$ and CO ΔE_{S-T} excitation energy (Fig. 1), similar to the linear relationship between CO/Pt(111) $\Delta E_{\text{top-fcc}}$ site preference energy and the energy of the CO $2\pi^*$ for the Pt(111) adsorption observed by Kresse and co-workers.¹¹ A linear fit also describes well the behavior of chemisorption energies on the seven other substrates included in the present work. Since the CO triplet state is produced by an excitation of an electron from the 5σ orbital to the $2\pi^*$ orbital, the singlet-triplet excitation energy is closely related to the $5\sigma-2\pi^*$ gap and to the position of the $2\pi^*$ orbital. This gives rise to a similar linear dependence of E_{chem} on the energy of CO $2\pi^*$ orbital and on ΔE_{S-T} .

Coupled-cluster¹⁴ and CI (Ref. 15) quantum chemical calculations accurately reproduce the experimental ΔE_{S-T} of 6.095 eV.²² On the other hand, regardless of the pseudopotential set, our DFT-GGA calculations always

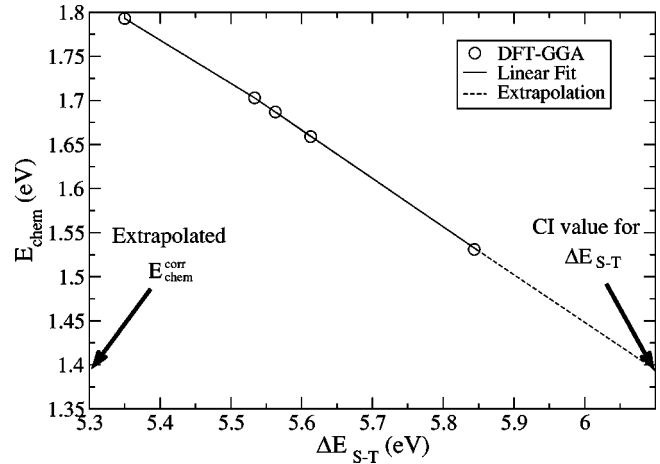


FIG. 1. $E_{\text{chem}}^{\text{hcp}}$ for CO on Pt(111) vs ΔE_{S-T} of CO for five pseudopotential sets (circles). Similar clear linear relationships are also obtained for other sites and metal surfaces. First-principles extrapolation procedure: $E_{\text{chem}}^{\text{GGA}}$ and $\Delta E_{S-T}^{\text{GGA}}$ values are plotted and fit to a line (solid). This line is extended to the abscissa representing $\Delta E_{S-T}^{\text{CI}}$. The corresponding ordinate value is $\Delta E_{\text{chem}}^{\text{corr}}$. Chemisorption on the hcp site of Pt(111) is used in this example.

predict a ΔE_{S-T} that is too small. The correct chemisorption energy $E_{\text{chem}}^{\text{corr}}$ can be obtained by using the relationship between E_{chem} and ΔE_{S-T} and extrapolating to the CI ΔE_{S-T} value,

$$E_{\text{chem}}^{\text{corr}} = E_{\text{chem}}^{\text{GGA}} + (\Delta E_{S-T}^{\text{CI}} - \Delta E_{S-T}^{\text{GGA}}) \frac{\delta E_{\text{chem}}^{\text{GGA}}}{\delta \Delta E_{S-T}^{\text{GGA}}}, \quad (1)$$

where $\Delta E_{S-T}^{\text{CI}}$ and $\Delta E_{S-T}^{\text{GGA}}$ are, respectively, the CI and GGA CO singlet-triplet excitation energies, and $\delta E_{\text{chem}}^{\text{GGA}} / \delta \Delta E_{S-T}^{\text{GGA}}$ is the slope of the fit of E_{chem} versus ΔE_{S-T} .

A universal feature of the corrected chemisorption energies presented in Table II is that they all indicate weaker chemisorption than the corresponding uncorrected values, with the $E_{\text{chem}}^{\text{corr}}$ values for the preferred site demonstrating much better agreement with experimentally determined adsorption energies. For example, the $E_{\text{chem}}^{\text{GGA}}$ for the experimentally seen CO/Pd(111) hollow site is 1.96 eV, as compared to 1.47–1.53 eV obtained by temperature programmed desorption measurements.²³ This rather large 0.46 eV error is eliminated by the use of the extrapolation, with $E_{\text{chem}}^{\text{corr}}$ of 1.60 eV, in very close agreement with experimental results. For the experimentally observed top site on Cu(111) the results are less dramatic but still noticeable, with $E_{\text{chem}}^{\text{GGA}}$ of 0.746 eV changed to $E_{\text{chem}}^{\text{corr}}$ of 0.621 eV in better agreement with the experimental value of 0.49 eV.²⁴ Overall, comparison of PBE and corrected results shows an improvement from 0.38 eV (30%) average overestimation for the PBE functional to 0.16 eV (13%) average error for our corrected results.

Examination of the data in Table II shows that there is a strong correlation between the magnitude of the correction and the chemisorption site. This is due to the different strengths of the metal-CO interactions in different local ge-

TABLE II. Results of linear regression of chemisorption energy versus singlet-triplet splitting energy. The smallest correlation coefficient of all linear fits is greater than 0.95. The DFT-GGA values for the chemisorption energies are given, along with the corrected energies obtained by extrapolation. Positive value of E_{t-h} indicates that top site is preferred. For each substrate, the site found to be preferred by experiment is marked with an asterisk (*). Experimental values for E_{chem} are: 1.43-1.71 for Pt(111), Refs. 28-30, 1.43-1.65 for Rh (111), Refs. 31, 32, 1.47-1.54 for Pd(111), Refs. 35, 23, 0.46-0.52 for Cu(111), Refs. 33, 34, 1.62-2.18 for Pt(100), Refs. 36-38, 1.24-1.65 for Rh(100), Refs. 39,40, 1.3-1.71 for Pd(100) Refs. 38,41, and 0.55-0.57 for Cu(100), Refs. 42, 43.

	Site	Slope	E_{chem}^{GGA}	E_{chem}^{corr}	Δ
Pt(111)	Top*	-0.211	1.717	1.560	-0.157
	Bridge	-0.435	1.758	1.433	-0.325
	hcp	-0.532	1.793	1.397	-0.396
	E_{t-h}	0.321	-0.076	0.164	0.240
Rh(111)	Top*	-0.259	1.866	1.673	-0.193
	Bridge	-0.456	1.920	1.581	-0.339
	hcp	-0.559	2.059	1.644	-0.415
	E_{t-h}	0.300	-0.193	0.030	0.223
Pd(111)	Top	-0.185	1.385	1.247	-0.138
	Bridge	-0.399	1.784	1.487	-0.297
	hcp*	-0.535	1.962	1.602	-0.360
	E_{t-h}	0.350	-0.577	-0.355	0.222
Cu(111)	Top*	-0.169	0.746	0.621	-0.125
	Bridge	-0.329	0.822	0.576	-0.246
	hcp	-0.375	0.889	0.610	-0.279
	E_{t-h}	0.206	-0.143	0.011	0.154
Pt(100)	Top*	-0.212	1.954	1.796	-0.158
	Bridge*	-0.422	2.139	1.824	-0.315
	Hollow	-0.607	1.698	1.246	-0.452
	E_{t-h}	0.395	0.256	0.551	0.295
Rh(100)	Top*	-0.246	1.905	1.723	-0.182
	Bridge*	-0.427	2.092	1.774	-0.318
	Hollow	-0.651	2.087	1.603	-0.484
	E_{t-h}	0.405	-0.182	0.120	0.302
Pd(100)	Top	-0.196	1.494	1.348	-0.146
	Bridge*	-0.384	1.927	1.641	-0.286
	Hollow	-0.583	1.937	1.503	-0.434
	E_{t-h}	0.387	-0.443	-0.155	0.288
Cu(100)	Top*	-0.170	0.830	0.703	-0.147
	Bridge	-0.286	0.834	0.620	-0.214
	Hollow	-0.523	0.831	0.441	-0.477
	E_{t-h}	0.353	-0.001	0.262	0.263

ometries. While the chemisorption bond is formed through both σ donation and π^* back donation, the contribution of π^* back donation to the adsorption bonding in the systems considered here is dominant because the fillings of the late transition metals studied here are greater than half.²⁵ The back-donation mechanism is strongly enhanced by going from top site to polycoordinated adsorption sites.^{11,20,26,27} Accordingly, the incorrect DFT-GGA ΔE_{S-T} (or the incorrect placement of the $2\pi^*$ orbital) will require the smallest correction for E_{chem} of the top site, followed by the bridge site,

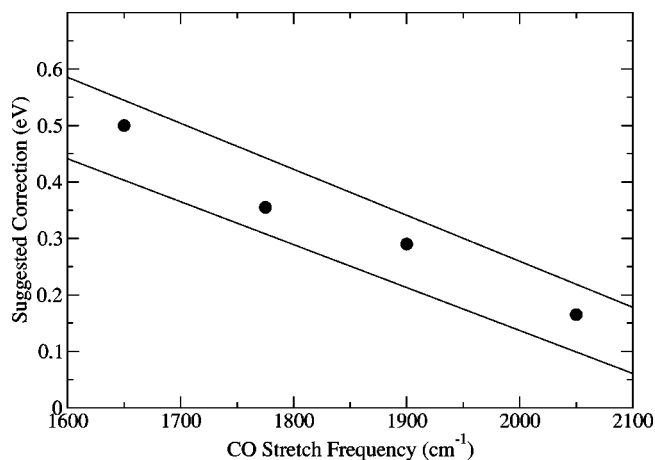


FIG. 2. Graphical guide for estimating E_{chem}^{GGA} from CO stretch frequency. Correction energy as a function of the adsorbed CO stretch frequency provides a simpler, more user-friendly method of applying the correction. Lines represent boundaries for suggested correction values, average correction values for high-symmetry sites for our highest quality DFT-GGA results in this study are shown as circles.

the threefold hcp hollow site on the (111) surfaces and the fourfold hollow on the (100) surfaces. This ranking is evident in the tabulated results. In the chemical language, the CO bond weakening is smallest for the top site and largest for the fourfold hollow site.

The DFT-GGA errors in the prediction of the preferred site are a direct outcome of the unequal treatment of the CO bond weakening at the top and hollow sites due to the unrealistically small ΔE_{S-T} and low $2\pi^*$ energy. Using our first-principles extrapolation to eliminate the CO bond weakening errors, our corrected DFT results give the highest value of E_{chem}^{corr} for the experimentally observed sites in all cases. For Pt(111), our raw DFT data show an incorrect site preference with an energy of 0.076 eV. The corrected energies agree with experimental site preference²⁸⁻³⁰ with an energy difference of 0.163 eV. Likewise, our raw DFT data disagree with experimental site preference^{31,32} while our corrected energies are in agreement. For Cu(111) the use of the correction gives the experimental site preference,^{24,33} though the corrected DFT results predict small (≤ 0.1 eV) differences between the top, bridge and hollow sites. Both the raw DFT and the corrected results for Pd(111) agree with the site preference observed by experiment.^{23,34,35} Our corrected results for the (100) surfaces agree with experimentally observed preferred adsorption sites for Pt (Refs. 36-38), Rh (Refs. 39,40), Pd (Refs. 38,41), and Cu (Refs. 42,43).

A less exact but simpler correction can be extracted from our data and applied to any CO/metal surface system. The data in Table II show that for any given site the $\delta E_{chem}^{GGA}/\delta \Delta E_{S-T}^{GGA}$ values and the consequent correction energy are fairly constant with scatter of about 0.1 eV across a range of systems.

As discussed above, the similarities for the same site and

the differences among the sites are consequences of the different degrees of CO bond weakening. The degree of CO bond weakening can be estimated from the frequency shift of adsorbed CO relative to the gas phase CO molecule, which can be easily calculated for any system. Then the frequency can be compared to those of top (typically 2000–2100 cm^{-1}), bridge (1850–1950 cm^{-1}), hcp (1750–1800 cm^{-1}) or fourfold hollow (1600–1700 cm^{-1}) sites and a corresponding correction applied.

For example, for CO adsorption on Ni(111), DFT-GGA calculations with PBE or PW91 functionals find the preferred site to be hcp or fcc,⁴⁴ in agreement with experimental results.⁴⁵ However, the E_{chem} are in 1.9–2.0 eV range, in contrast to experimental E_{chem} of 1.12–1.55 eV. Since the hollow site CO/Ni(111) stretch frequency of 1800 cm^{-1} (Ref. 44) is similar to the 1830 cm^{-1} frequency for CO on Pd(111) hollow site,²¹ we expect the E_{chem} error to be similar, and the corrected value of E_{chem} is about 1.55 eV, in much better agreement with experimental results. A graphical representation of the suggested correction to E_{chem} as a function of CO stretch frequency is given in Fig. 2.

IV. CONCLUSION

We have shown that the chemisorption energies of CO adsorbed on metal surfaces depend linearly on gas-phase CO singlet-triplet splitting. The difference between the high-level quantum chemistry coupled-cluster/CI and DFT-GGA

singlet-triplet excitation energies can then be used to extrapolate to chemisorption energies with the CO error removed. The corrected values are in good agreement with experimental results. The correction also eliminates the GGA errors in site preference. We find a strong correlation between the amount of CO bond breaking and the correction magnitude. This suggests that an estimate of the GGA error due to the incorrect description of CO electronic structure can be readily obtained through the frequency shift of adsorbed CO at any site on a metal surface. The demonstrated method should be applicable to various adsorption systems where the charge transfer responsible for chemisorption is sensitive to the adsorbate electronic structure.

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