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Correlations in coverage-dependent atomic adsorption energies on Pd(111)

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The adsorption energy of an adsorbate can depend strongly on its coverage. We present density-functional calculations of the adsorption energy of C, N, and O on the fcc sites of Pd(111) at coverages from 0.2 to 1 ML. The adsorption energy generally increases (gets weaker) with coverage in a near linear fashion for the most stable configurations. We observed a practically constant *d*-band filling at all coverages and interpret the coverage dependence in terms of a simple *d*-band model where the *d* band is broadened and lowered in energy by the interaction with the adsorbates. We find the Pd(111) *d*-band center is approximately linearly correlated with the coverage of each adsorbate. A consequence of this electronic structure-coverage correlation for each adsorbate is that the adsorption energies of each adsorbate configuration are strongly correlated with each other. All of the exceptions to these correlations can be traced to surface reconstruction or adsorbate configurations that are not geometrically similar to adsorption in the fcc hollow sites. Finally, we show that all the coverage-dependent adsorption energies can be collapsed into a single configurational correlation by scaling of the adsorption energies.

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I. INTRODUCTION

Adsorption on metal surfaces is one of the first steps in a heterogeneously catalyzed reaction. The rate of a surface reaction is dependent in a trivial way on the coverage of adsorbates from simple mass-action rate laws. A more subtle effect of coverage on reaction rates is that the reaction barriers can be coverage dependent, in essence meaning the rate parameters are coverage dependent. There are several ways reaction rates can show coverage dependence. First, the adsorption energy of an adsorbate is often dependent on the coverage due to bonding competition with the surface, or repulsive interactions between the adsorbates.[1] This can affect the thermodynamics of surface reactions by changing the energy of the reactants or products. Second, reaction barriers are often related to the energies of the reactant or product. For example, the oxygen dissociation barrier is linearly related to the adsorption energy of the atomic oxygen adsorbates.[2] Consequently, modifications of the adsorption energy of the atomic adsorbates by changes in coverage are expected to also change the oxygen dissociation or desorption barrier. At higher coverages the dissociation barrier is expected to be higher because the adsorption energies get weaker at high coverages. Finally, surface diffusion barriers could change as coverage changes resulting in coverage-dependent adsorbate mobilities.

The coverage dependence of the adsorption energy can be calculated using density-functional theory. For example, Todorova *et al.*[3,4] examined the coverage dependence of oxygen adsorption on several 4*d* transition metals from Ru to Ag. Oxygen on Rh(111),[5] on Cu(111),[6] and Ag(111) (Ref. 7) has also been examined, as well as nitrogen on Cu.[8] In these studies the coverage dependence was examined by calculating the adsorption energy of a few (4–10) typical coverages between 1/8 and 1 ML (monolayer defined as one adsorbate per metal atom). In many adsorption systems, thin surface oxides[9,10] or nitrides,[8] or sulfides[11] can form that resemble neither the bulk phases, nor the simple surface adsorbate phases. These are beyond the scope of this paper.

We recently found the trends in the coverage-dependent adsorption energies of atomic oxygen on Pt and Au(111) could be simply explained by the adsorbate-induced changes to the surface electronic structure.[12] In that work we also found that the similarities in the adsorbate-induced changes to the surface electronic structure of Pt and Au(111) on the different metals led to a strong correlation of the coverage-dependent properties on the two surfaces. In this work we expand this principle to other atomic adsorbates, C, N and O, on Pd(111).

We focus exclusively on the coverage dependence of the adsorption energy of atomic adsorbates (C, N, and O) in threefold fcc adsorbate sites on Pd(111) and their effects on the surface electronic structure. We first present the coverage-dependent atomic adsorption energies for each adsorbate and show how the surface electronic structure is perturbed in a similar way by each adsorbate. We then discuss how the similar electronic structure modification leads to correlations between the coverage-dependent adsorption energies of each adsorbate. We conclude with a discussion of the significance and limitations of these configurational correlations.

II. METHODS

We used density-functional theory to calculate the adsorption energy of each adsorbate using the plane-wave code DACAPO (Ref. 13) with Vanderbilt ultrasoft pseudopotentials[14] generated for the PW91 (Ref. 15) exchange correlation functional. Details of the Pd pseudopotential can be found in Ref. 16; the default pseudopotentials for C, N, and O were used. The PW91 (Ref. 15) exchange-correlation functional was used. The adsorption is modeled on four layer slabs with the bottom two layers fixed at the bulk lattice coordinates (Pd lattice constant calculated to be 3.92 Å, in good agreement with the experimental value of 3.88 Å and other calculated values),[17] and the top two layers and adsorbates were unconstrained. The slabs were separated by approximately 10 Å of vacuum space. The dipole correction[18] was found to have a negligible effect on these calculations and was not used in this work. The geometries were optimized using a quasi-Newton algorithm until the forces were below 0.05 eV/Å. Each adsorption energy was explicitly converged with respect to plane waves and k-point sampling until the variation with respect to these parameters was less than 0.02 eV/adsorbate. This typically required plane-wave cutoffs in excess of 375 eV and k-point grids with a density similar to a $14\times 14\times 1$ grid in a 1×1 surface unit cell. The adsorption energy was calculated as $\Delta H_{\text{ads}}(\text{eV/ads})=\frac{1}{N_{\text{adsorbate}}}(E_{\text{slab+adsorbate}}-E_{\text{slab}}-N_{\text{adsorbate}}E_{\text{adsorbate}})$, where E_x represents the total energy as calculated by DFT of the relevant system (slab, slab+adsorbate or adsorbate) and $N_{\text{adsorbate}}$ is the number of adsorbates. In this definition a negative adsorption energy is exothermic. The adsorbate energy was calculated for a gas-phase atom in a 10 Å×10 Å×10 Å box surrounded by vacuum in a spin-polarized calculation.

Coverages were examined on 20 different configurations for each adsorbate in fcc sites ranging from 0.2 to 1 ML. All adsorption energies are referenced to the gas-phase atomic state and no vibrational energy corrections in the adsorbed state have been made. The choice of atomic state is largely for convenience because some the standard states of the atomic adsorbates examined are gases and some are solids. The use of different choices of reference state will simply shift the adsorption energies in this work by a constant amount and will have no effect on the conclusions drawn.

The surface electronic structure has been calculated by projecting the total density of states onto atomic orbitals localized on each atom. The spatial extent of the atomic orbitals is infinite, which can lead to overlap of the orbitals on a particular atom with the orbitals of neighboring atoms. The overlap can result in double counting of electrons from neighboring atoms on the atom-centered orbitals. Consequently, it is convenient to define a cutoff radius to truncate the states within the atomic orbitals to limit the overlap. In this work we used a cutoff radius of 1 Å to truncate the orbitals. DACAPO also calculates the atom-projected density of states with no cutoff radius (termed the infinite cutoff radius). Qualitatively the trends are similar with the two cutoff radii, and only the results for the infinite cutoff radius are presented in this work. The d-band center is calculated as the first moment of the d band, and the d-band width as the square root of the second moment. The number of electrons in the d band is calculated by integrating the d band up to the Fermi level. The fractional d filling is defined by the number of d electrons in the band divided by 10 (the maximum possible number of d electrons in the d band of a single atom).

III. RESULTS AND DISCUSSION

A. Coverage-dependent adsorption energies

The adsorption energy of each adsorbate is presented as a function of coverage in Fig. 1. Generally, the adsorption energy increases (gets weaker) as the coverage increases. The adsorption energy is not a simple function of coverage. Different configurations with the same overall coverage have different adsorption energies due to differences in the interactions between the adsorbates. With the atomic gas-phase reference state the trend in adsorption energies is generally C>N>O for nearly all coverages. There were two exceptional points for the carbon data set due to substantial surface reconstructions that occurred. These two points are discussed later in the paper. The range of adsorption energies with coverage is significant, spanning nearly 1.5 eV from low coverages near 0.2 ML to a fully covered 1 ML coverage.

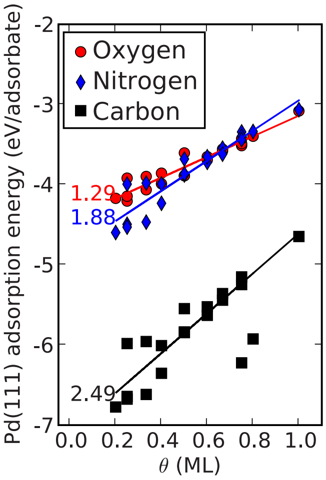

FIG. 1. (Color online) Coverage dependence of C, N, and O on Pd(111). Multiple configurations for some coverages are shown. The drawn lines represent best fits to the most stable configurations. The two outlier points near 0.8 ML on C were not included in the fit and are discussed in the text. The slope of each linear fit to the most stable configurations is shown in color to the left of each set of data.

The dependence of the adsorption energies on coverage varies systematically from C to O. Carbon is the most sensitive with $d\Delta\text{H}_{\text{ads,C}}/d\theta=2.49$ eV/ML. Nitrogen is less sensitive, $d\Delta\text{H}_{\text{ads,N}}/d\theta=1.88$ eV/ML and oxygen even less sensitive $d\Delta\text{H}_{\text{ads,O}}/d\theta=1.29$ eV/ML. As the number of valence electrons in the adsorbate increases, and the atomic size decreases, the interaction of the adsorbate with the metal surface decreases.

There are several interpretations of the coverage dependence. One interpretation is that the adsorbates repel each other by some mechanism (e.g., dipole interactions, Pauli repulsion, etc.). A second mechanism is bonding competition.[1] In the bonding competition mechanism we consider that the adsorbates compete for bonding with the surface as the coverage increases resulting in lower net bonding. We will show in the next section that the coverage dependence can be explained simply by the adsorbate-induced changes to the surface electronic structure. Our discussion is an alternative approach to the discussion in Ref. 1.

B. Coverage-dependent d-band structures

We now consider the effect of adsorption on the surface d-band structure. In the d-band model of adsorption[19–23] the interaction of atomic adsorbates with d metals is considered in two steps. In the gas phase the energy of an atomic orbital

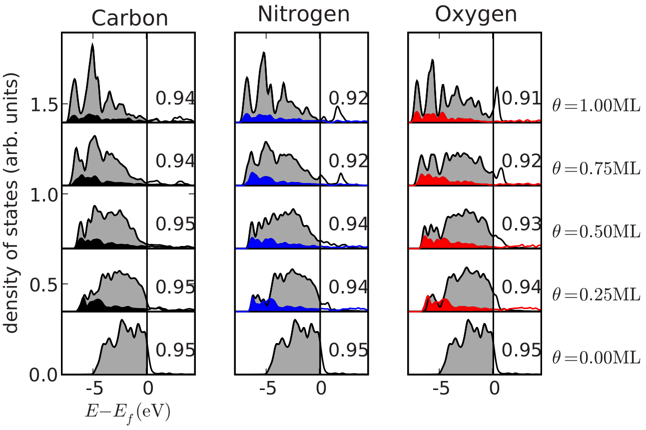

FIG. 2. (Color online) Adsorbate induced electronic structure changes of Pd(111) as a function of coverage for each adsorbate. The occupied Pd *d* band is shaded in gray, while the occupied adsorbate *sp* states are shaded in color. A vertical line indicates the Fermi level in each frame. The fractional *d*-band fillings are shown at each coverage.

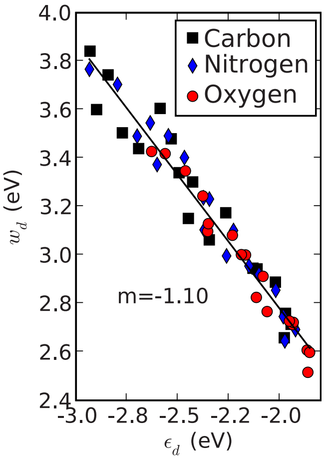

FIG. 3. (Color online) Correlation of the surface *d*-band center and *d*-band width for all configurations studied in this work. The correlation is consistent with a rectangular band model where the fractional filling of the *d* band is conserved when the band changes shape.

is very narrow in width (it is considered sharp). As the adsorbate approaches the metal surface, the energy of the atomic orbital begins to broaden and lower in energy through interactions with the surface s,p electron band, which is very broad in energy (many electron volts in width) and featureless. As the adsorbate approaches the surface more closely it begins interacting with the surface *d* band. In contrast to the broad s,p electron band, the surface *d* band is considerably narrower and sharper in energy (a few electron volts in width). The narrowness in energy causes a strong interaction with the adsorbate orbitals which split into bonding and antibonding states. The splitting of these levels is largely determined by the position of the *d* band in energy, which is typically approximated by the *d*-band center. The closer the *d*-band center is to the Fermi level the stronger the adsorbate bond is because the antibonding state is usually above the Fermi level and thus unoccupied. As the *d*-band center moves away from the Fermi level the antibonding atomic state can move below the Fermi level and become occupied resulting in a weaker bond. In the simple *d*-band model it is assumed that the *sp* bands of the transition metals are largely similar, and that variations in adsorption behavior are dominated by changes in the *d* band.

Adsorption strongly affects the surface *d*-band structure as shown in Fig. 2. This means that adsorbates interact differently with the surface *d* band when there are adsorbates present then with the clean surface. In other words, the interaction with the surface *d* band is coverage dependent. In Fig. 2 we show the surface Pd *d* band at several different coverages for each adsorbate. The surface *d* band gets broader as the coverage increases due to the interactions (hybridization) of the *d* band with the adsorbates. The fractional filling of the *d* band remains essentially constant, and as a consequence the average energy of the *d* band (the *d*-band center) must decrease. We note that there is some evidence that small fractions of electrons are transferred out of the *d* band at the highest coverages based on changes in the integrated *d* filling, consistent with oxidation (i.e., loss of electrons) of the surface. The atom-projected density of states with a short cutoff radius of 1 Å shows a more significant reduction in electrons in the band (approximately 0.1 fewer electrons in the *d* band at 1 ML than at 0 ML for each adsorbate). We cannot quantitatively estimate the magnitude or significance of these charge transfers due to limitations in the algorithm used. The choice of cutoff radius is arbitrary; too short a radius and charge polarization may appear to be charge transfer, while too long a radius may overcount electrons belonging to neighboring overlapping orbitals. The general trend is, however, independent of the cutoff radius choice provided a consistent radius is used. We show next that the modifications of the *d* band are largely due to changes in the band shape and that charge transfer is not required to explain the majority of the modification.

Despite the apparent minor decrease in the *d*-band filling in Fig. 2, we find that the *d*-band width and *d*-band center are highly correlated with each other, as shown in Fig. 3. This is consistent with a simple rectangular band model with a constant *d*-band filling. There is some scatter in these results, so we cannot definitively say there is no charge transfer, only that it is not necessary to explain our results.

The dependence of the *d*-band center on coverage varies with each adsorbate. The *d*-band center is plotted as a function of coverage for each configuration of each adsorbate in Fig. 4. The dependence of the surface electronic structure on the adsorbate is consistent with the adsorption energy dependence observed in Fig. 1; weaker adsorption energies correlate with more negative *d*-band centers. The carbon adsorption energy showed the most sensitivity to coverage. Carbon is also the most strongly bonding adsorbate and the one that has the strongest modification of the surface electronic structure.

In alloy systems, the width of the *d* band is related to the overlap of neighboring *d* orbitals.[24] The same mechanism applies to the width of the *d* band when the neighboring, overlapping orbitals are from adsorbates. Here the broadening of the surface *d* band is due to increased overlap between

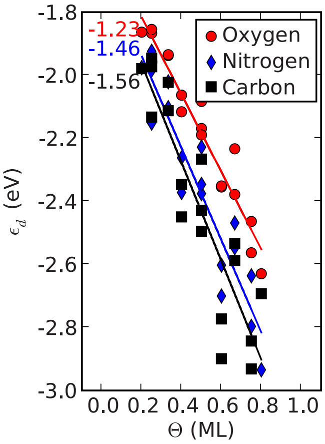

FIG. 4. (Color online) Coverage-dependent surface electronic structure modifications.

the adsorbates and the surface *d* orbitals due to the adsorbate bonds. The amount of overlap is partially determined by the distance between the adsorbate orbitals and the *d* orbitals. One expects that adsorbates farther from the surface will cause less broadening, and be less sensitive to coverage effects. The height of the adsorbates from the surface is plotted in Fig. 5. These results first show that the average height of an adsorbate tends to increase as the coverage increases. This is nominally consistent with the weakening of the adsorbate bonds. Second, the results show that carbon, the largest adsorbate which bonds most strongly, is also the closest to the surface resulting in the most overlap with the *d* orbitals and correspondingly is the most sensitive to coverage effects. Nitrogen is intermediate in behavior and oxygen (the smallest adsorbate) shows little dependence of the adsorbate height with coverage.

C. Configurational correlations in coverage-dependent adsorption energies

The common adsorbate-induced electronic structure mechanism between these adsorbates implies that there could be correlations between the adsorption energies of each adsorbate at each coverage. We demonstrate this in Fig. 6 where the adsorption energy of each configuration of C and N is plotted against the same configuration of O. A series of near linear correlations are observed. We have previously found that the adsorption energy of oxygen on Au and Pt display similar configurational correlations as observed here with similar adsorbate-induced electronic structure mechanisms.[12] Here we show that the configurational correlation is a more general concept that applies to other adsorbates and metals too.

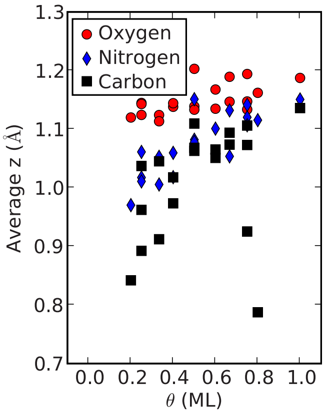

FIG. 5. (Color online) Variations in the height of the adsorbates due to coverage. Adsorbate heights tend to increase with increasing coverage. The exceptions from carbon are due to reconstruction artifacts.

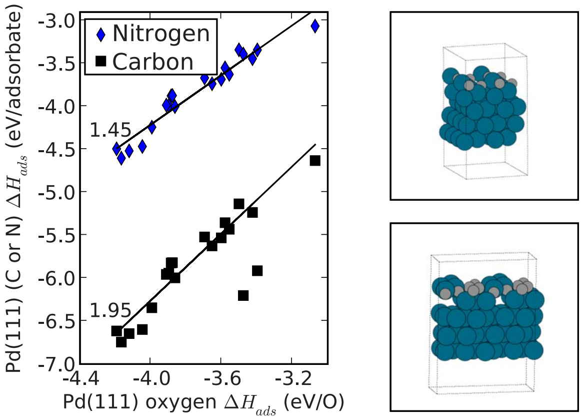

FIG. 6. (Color online) Configurational correlations of C and N with O on Pd(111). The points that fall off the correlation for carbon are geometrically dissimilar structures that massively reconstructed and incorporated carbon into the surface while optimizing the geometry as shown in the subfigures. The slopes of the best fit lines are shown to the left of each correlation. The two outliers for carbon were not used in the fit.

The configurational correlations in this work rely on all the configurations being geometrically similar. The most notable exceptions to the correlations we observed in this work were two configurations of carbon that resulted in a significant reconstruction of the surface upon relaxation. These reconstructed surfaces may be examples of a thin film that is more stable than a simple adsorbate structure, similar to the thin oxide films sometimes observed.[10] We did not consider these structures further or for any of the other adsorbates in this work. The remaining small deviations from the correlations shown in Fig. 6 can largely be explained by small deviations of the adsorbate positions from the ideal fcc site positions.

The correlations are evidently independent of the exchange-correlation functional used. We calculated the adsorption energies non-self-consistently[20] with the LDA exchange function of Vosko, Wilk, and Nusair (VWN),[25] the GGA function of Perdew, Burke, and Ernzerhof (PBE),[26] the revised PBE (revPBE) functional,[27] and the alternate revision of PBE (RPBE) (Ref. 20) exchange-correlation functionals using the frozen self-consistent PW91 electron densities. The total energy is variational in the electron density, thus near the ground-state, self-consistent electron density small variations in the density are not expected to result in significant errors in the energy calculations. The non-self-consistent adsorption energies are plotted against the self-consistent ener-

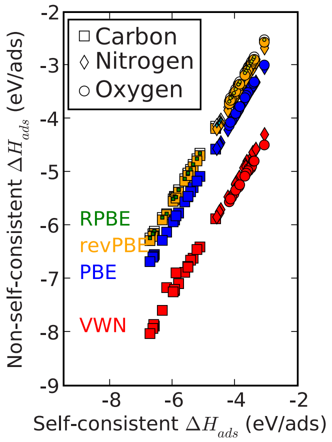

FIG. 7. (Color online) Correlations in the adsorption energy for each adsorbate calculated non-self-consistently with different exchange-correlation functionals.

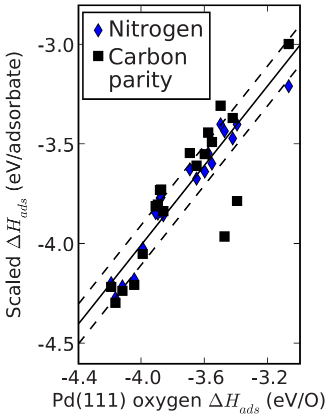

FIG. 8. (Color online) Reduced configurational correlations for C and N with O on Pd(111). The dashed lines show a range of ±100 meV from parity. The two outliers for C are due to the reconstructions observed for those configurations which make them geometrically dissimilar to the other configurations considered.

gies in Fig. 7. Remarkably the adsorption energies are highly correlated, and the trends observed self-consistently are also observed in the non-self-consistent data. The majority of the data in Fig. 7 lies within 50 meV of a linear fit to each data set, which is within a factor of 2 of the convergence errors in this work. Two exceptions to the correlations are the two reconstructed C structures which showed significant deviations (~250 meV) with the VWN(LDA) functional. The gradients in electron density at the surface of these structures are expected to be much greater than the adsorbate structures due to the reconstructions, and consequently the local-density approximation (LDA) adsorption energies show less correlation with the generalized gradient approximation (GGA) adsorption energies for these structures.[19] Significantly smaller deviations were observed between the three GGA functionals examined for these reconstructed surfaces.

We expect that similar configurational correlations could be observed with hcp sites, mixed site occupations, different metal surfaces, and perhaps mixed adsorbates provided that the configurations remain geometrically similar across different adsorbates and surfaces and that similar bonding mechanisms are active. We do not expect these types of correlations to exist when there are different bonding mechanisms (e.g., dipole interactions, hydrogen bonding, or dimer formation) between the configurations or when there are no *d* orbitals (e.g., in Al), or the *d* orbitals do not participate significantly in the bonding mechanism.

D. Principle of corresponding adsorption states

Two linear correlations in the same variable are themselves linearly correlated. Thus, each of the configurational correlations in Fig. 6 can be reduced into a single correlation that describes the coverage dependence and configurational correlation of all of the adsorbates with oxygen on Pd(111). We subtracted the intercept of each linear fit to each correlation in Fig. 6 and scaled each correlation by the reciprocal slope of the linear fit to collapse all the data into a single correlation shown in Fig. 8. The result is a near linear correlation of the reduced adsorption energies of C and N with that of O on Pd(111). In virtually every case the deviation from linearity is less than 100 meV/adsorbate and in many cases less than 50 meV/adsorbate. The significance of this data reduction is that we can use it to predict the adsorption energy of other adsorbates on Pd(111) if the slope and intercept of the configurational correlation can be identified from two calculations, e.g., at 0.25 and 1 ML.

These correlations of coverage-dependent atomic adsorption phenomena can likely be generalized to more complex adsorbates and to trends in catalytic activity. Nørskov and co-workers[28] recently reported scaling relations for the adsorption of C, N, O, and S and the hydrogenated versions of these adsorbates at a single coverage on many transition metal surfaces. Those authors reported similar scaling relations for oxide, nitrides, and sulfides[29] and for trends in catalytic activity.[30] It is likely that these other reported scaling relations are valid at other coverages as shown in this work.

IV. CONCLUSIONS

We have shown that the coverage dependence of atomic C, N, and O adsorption on Pd(111) shows similar behaviors, in all cases with adsorption energy weakening with coverage. The coverage dependence was attributed to a coverage-dependent adsorbate-induced surface electronic structure modification. The overlap of the adsorbate orbitals with the surface *d*-band results in a broadening of the surface *d* band and a lowering of the surface *d*-band center and a consequent weakening of subsequent adsorbate bonds. The extent of the adsorbate-induced broadening was linked to the size of the atomic adsorbates and the low-coverage adsorption energy. Larger first-row adsorbates tended to bond more strongly to the surface and have a bigger effect on the surface electronic structure. The common electronic structure modification mechanism led to a set of near linear correlations between the adsorption energies of all the configurations considered on each surface. The near linearity of these correlations enabled us to scale each correlation to collapse them into a single correlation.

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