

# Electronic Composition–Property Relationship Applied to SO<sub>2</sub> Chemisorption on Pt(111) Surfaces, Alloys, and Overlayers

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We have developed a new electronic composition–property relationship between the adsorption energy of molecules binding unequally to multiple atoms on metal surfaces and the electronic properties of the surface. This relationship allows the estimation of the relative stability of adsorbates on various surfaces, assuming that the adsorbate adopts the same local configuration on each surface, and therefore also allows the estimation of the adsorption energy of molecules through large regions of parameter space in alloy systems with data from only a few explicit calculations. We have applied this relationship to the adsorption of SO<sub>2</sub> on Pt surfaces alloyed with Pd, Cu, Ru, and Ni. Using a new formula for weighting the metal d-band, we found a strong linear relationship between the weighted positions of the d states of surfaces and the most stable molecular adsorption energies. The consequences of our electronic composition–property relationship for catalyst design are also discussed.

## Introduction

It is well-known that the catalytic properties of alloys are often superior to those of pure metals because of either the electronic effect or the ensemble effect or both.<sup>1</sup> The difficulty, however, with choosing an alloy with desired properties is that the range of parameter space becomes drastically larger when alloys are explored versus pure metals. If a generally applicable approach could be found such that the properties of reactions could be predicted on different surfaces, such as monometallic surfaces, alloy surfaces, and overlayers, our ability to design catalysts would be augmented tremendously. The d-band center and weightings thereof have been found to correlate well with the chemical activity of metal surfaces,<sup>2–5</sup> but so far the weightings are suitable only for predicting the interactions of simple adsorbates in a limited way, e.g., with a single type of metal atom on monometallic or pseudomorphic overlayer surfaces, such as the adsorption of CO at the top site of Pt(111) or Cu/Pt(111),<sup>4</sup> or of interactions between adsorbates and surfaces on which the adsorbates form bonds equally with more than one type of metal surface atom, such as hydrogen chemisorption on the hollow site of Pd–Re alloyed overlayers and alloyed surfaces.<sup>6</sup>

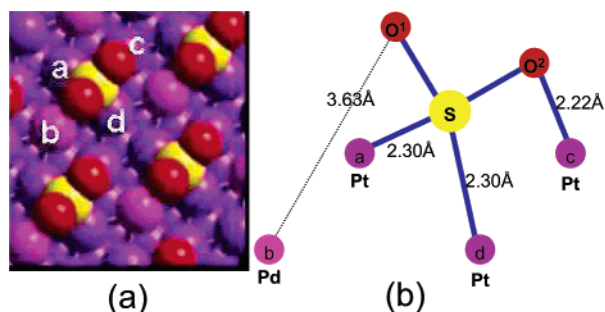
In this Letter, we present a model that can be used to predict the binding strength of chemisorbed molecules which bind unequally to multiple types of surface atoms. The adsorption of SO<sub>2</sub> on the Pt(111) surface, alloy surfaces, and overlayers, is used as an example of such adsorption processes and a means to verify our model. The chemistry of sulfur-containing species on transition metal catalysts has been of interest to scientists for decades, because it is critical in poisoning the catalysts under

both oxidizing and reducing conditions.<sup>7–9</sup> A fundamental understanding of properties of metals surfaces that govern their interactions with SO<sub>2</sub> could shed light on the design of sulfur resistant transition metal catalysts. Moreover, a successful approach to modeling SO<sub>2</sub> should lead to the ability to model a variety of molecules with significant interest to catalysis and surface physics.

## Computational Details

With the GNU publicly licensed software DACAPO,<sup>10</sup> first principles density functional theory (DFT) methods were used to study the adsorption of SO<sub>2</sub> on various alloyed surfaces and overlayers. The initial geometries of SO<sub>2</sub> on all the surfaces were chosen from the most stable adsorbed configuration (fcc  $\eta^2$ -S<sub>b</sub>O<sub>a</sub>) on the clean Pt (111) surface, determined in one of our previous studies.<sup>11</sup> In this geometry, SO<sub>2</sub> is at an fcc site with two atoms (S and O<sup>2</sup>) down and one atom (O<sup>1</sup>) sticking up, as illustrated in Figure 1. To compare the relative stability of SO<sub>2</sub> on different surfaces, a (2 × 2) unit cell and a three-layer slab model were used throughout the study. The use of a three-layer thick and (2 × 2) Pt slab model to describe accurately the properties of atomic and molecular adsorbates has been tested as explained by publications from our group and from others.<sup>4,6,11–16</sup> The positions of the atoms in SO<sub>2</sub> and those in all but the bottom Pt layer in the slab model were relaxed during the optimization. The bottom Pt layer was fixed at the calculated bulk lattice constant, 4.00 Å. A vacuum of ~10 Å was used to separate the slabs. The gradient-corrected exchange-correlation functional PW91-GGA<sup>17</sup> was used, in addition to ultrasoft pseudopotentials<sup>18,19</sup> and planewave expansions with an energy cutoff of 25 Ry (340 eV). All the surface Brillouin zones were sampled at 4 × 4 × 1 Monkhorst-Pack k-points.<sup>20</sup> Taking into

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**Figure 1.** Schematic of SO<sub>2</sub> adsorbed to alloyed Pt(111) surfaces in which the surface atom labeled b is replaced by another atom, Pd in this case: (a) top view; (b) side view with bond lengths of the Pd–Pt system.

account explicitly electron spin was found to change the SO<sub>2</sub> adsorption energies by only 0.1 kJ/mol on alloy surfaces, well within the numerical accuracy of the pseudopotential methods. Therefore, all the calculations were nonmagnetic in this study.

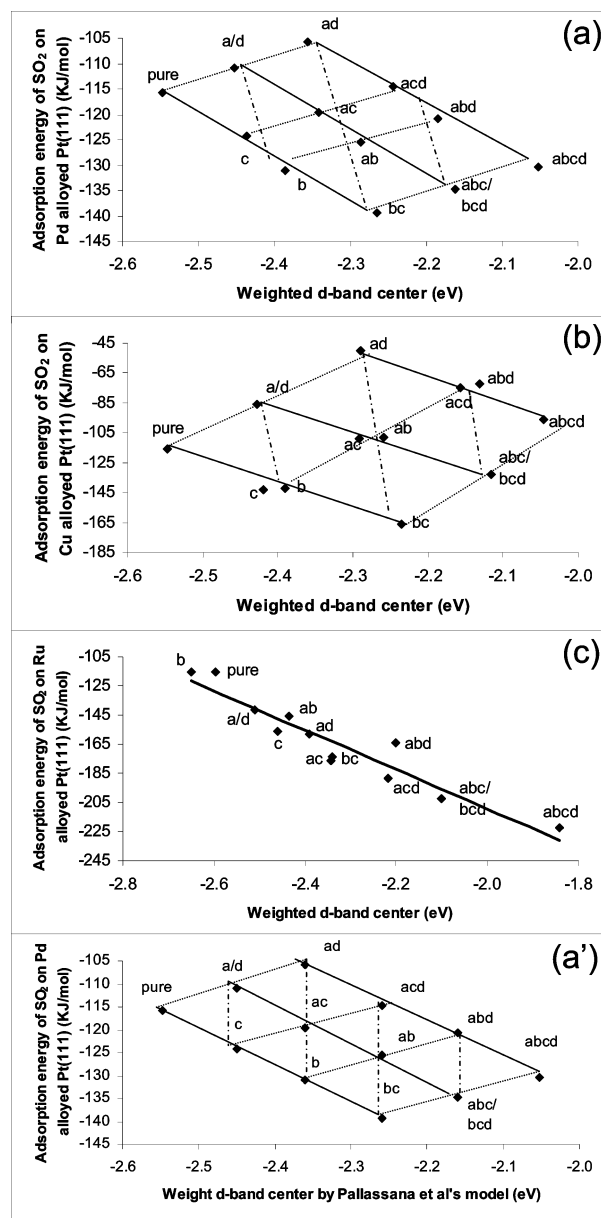
The surface alloys and overlayers, designated as  $nM^x/\text{Pt}(111)$ , were modeled by replacing  $n$  Pt atoms in the top Pt layer with other metal atoms (M) such as Pd, Cu, Ru and Ni etc.  $n = 1, 2$  or  $3$  are surface alloys with different local concentrations of M, such that  $n = 4$  is an overlayer;  $x$  represents the sites replaced, as marked in Figure 1 and Figure 2.

## Results and Discussions

For SO<sub>2</sub> adsorbed on  $nM^x/\text{Pt}(111)$  surfaces, the d-band position for Pt and M atoms on the surfaces varies with the types and concentrations of M atoms. The extent of overlap between the orbitals of SO<sub>2</sub> and the d-bands of the surface atoms therefore also varies. Because SO<sub>2</sub> binds unequally to multiple surface atoms (Figure 1), different arrangements ( $x$  in  $nM^x/\text{Pt}(111)$ ) of M atoms on the Pt(111) surface will have different effects on the adsorption energy of SO<sub>2</sub>. Considering all these factors, we constructed a simple expression for weighting the d-band center of various alloyed surfaces or overlayers as follows:

$$E_{d\text{-weighted}} = \frac{\sum_M V_M^2 E_d^M (\sum_i N^{M-i} S^{M-i})}{\sum_M V_M^2 (\sum_i N^{M-i} S^{M-i})} \quad (1)$$

where  $V_M^2$  is the d-band coupling matrix for the surface metal atom M, which has been tabulated as a database in Ruban et al.'s work ( $V_{\text{Pt}}^2 = 3.90$ ,  $V_{\text{Pd}}^2 = 2.78$ ,  $V_{\text{Cu}}^2 = 1.0$ ,  $V_{\text{Ru}}^2 = 3.87$ ,  $V_{\text{Ni}}^2 = 1.16$ , all relative to Cu).<sup>21</sup>  $E_d^M$  is the d-band center of the surface metal atom M. It was calculated by taking the first moment of the normalized d-projected density of states (pDOS) about the Fermi level.  $N^{M-i}$  is the number of bonds between the surface metal atom M and the atom  $i$  in the adsorbate molecule. [M and  $i$  are considered to be bonded in two possible ways: first, when the distance between M and  $i$  is shorter than 3 Å (such as in Figure 1,  $N^{a/d-S} = 1$ ,  $N^{c-O^2} = 1$ ); second, when the distance between M and  $i$  is long, but  $i$  has more than one geometrically equivalent atom M (such as in Figure 1,  $N^{b-O^1} = 3$ ).]  $S^{M-i}$  represents the bond strength between the surface metal atom M and the atom  $i$  in the adsorbate. Inclusion of  $S^{M-i}$  is an important, distinguishing element of our model.<sup>6</sup> It accounts for the differences in the interaction of different atoms in the



**Figure 2.** Adsorption energies of SO<sub>2</sub> on different alloyed Pt(111) surfaces and overlayers vs. the weighted d-band center of the surfaces: (a) Pd–Pt series; (b) Cu–Pt series; (c) Ru–Pt series; (a') Pd–Pt series (by Pallassana et al.'s model<sup>6</sup>).

adsorbate and different metal atoms ( $x$ ). We chose the form of  $S^{M-i}$  to be electrostatic:

$$S^{M-i} = \frac{C^M C^i}{d_{M-i}} \quad (2)$$

where  $C^M$  and  $C^i$  are the Pauling electronegativities of the metal atom (M) and the atom ( $i$ ) in the adsorbate,<sup>22</sup> and  $d_{M-i}$  is the distance between these two atoms (Figure 1b). The sum in eq 1 runs over all geometrically equivalent atoms M in the adsorbate-covered surface cell. It is found in our calculations that the change of geometry parameters  $d_{M-i}$  in going from adsorption on the pure metal to adsorption on alloys is about an order of magnitude more among different series than within each series. This is due to the effects of anti-segregation. Therefore, even though we fully relaxed each system aside from the bottom layer, we used the same set of geometry parameters ( $d_{M-i}$ ) for each  $nM^x/\text{Pt}(111)$  series (same M). The error for

**TABLE 1: Binding Energies (BE) of SO<sub>2</sub> on *n*M<sup>x</sup>/Pt(111) and Comparison of Weighted d-Band Center of the Surfaces Calculated by Our Model and Pallassana et. al.'s Model<sup>6</sup>**

M	Pd			Cu			Ru		
x	BE <sup>a</sup>	E <sub>d</sub> <sup>b</sup>	E <sub>d</sub> <sup>c</sup>	BE <sup>a</sup>	E <sub>d</sub> <sup>b</sup>	E <sub>d</sub> <sup>c</sup>	BE <sup>a</sup>	E <sub>d</sub> <sup>b</sup>	E <sub>d</sub> <sup>c</sup>
a/d	110.87	-2.45	-2.45	85.83	-2.43	-2.43	141.84	-2.46	-2.46
b	131.07	-2.39	-2.36	142.25	-2.39	-2.36	115.42	-2.60	-2.60
c	124.22	-2.44	-2.45	143.12	-2.41	-2.43	156.33	-2.41	-2.46
ab	125.58	-2.29	-2.26	108.22	-2.26	-2.23	145.59	-2.39	-2.35
ac	119.63	-2.34	-2.36	108.90	-2.28	-2.30	176.03	-2.29	-2.35
bc	139.31	-2.27	-2.26	166.64	-2.24	-2.22	173.96	-2.29	-2.34
ad	105.82	-2.36	-2.36	50.16	-2.29	-2.29	158.29	-2.34	-2.34
acd	114.60	-2.24	-2.26	75.25	-2.16	-2.16	188.51	-2.17	-2.23
abd	120.81	-2.19	-2.16	72.24	-2.14	-2.11	163.76	-2.15	-2.09
abc	134.70	-2.16	-2.16	133.04	-2.12	-2.11	202.22	-2.05	-2.08

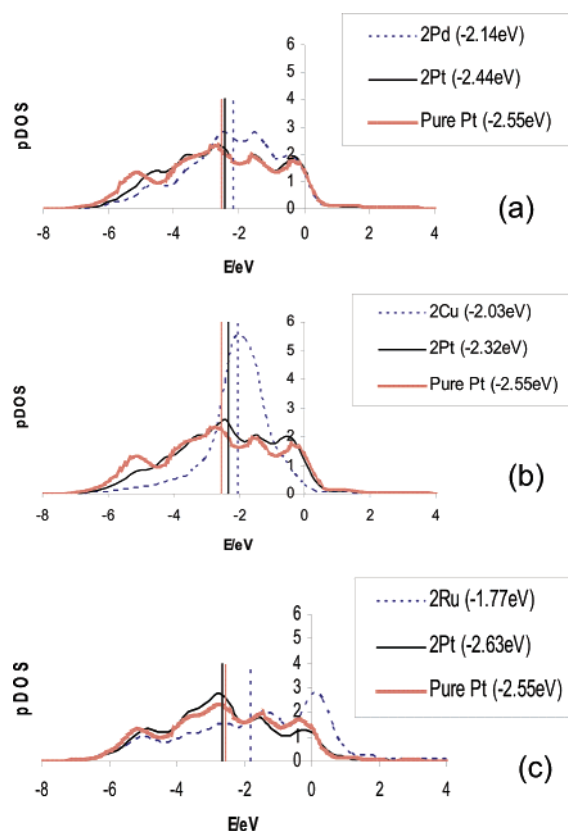
<sup>a</sup> Positive value is used here (unit: kJ/mol). <sup>b</sup> Calculated by our model in this manuscript (unit: eV). <sup>c</sup> Calculated by Pallassana et al.'s model in ref 6 (unit: eV).

$E_{d\text{-weighted}}$  caused by this approximation is less than 0.001 eV, which is considered to be negligible.

In Figure 2 are plotted the energies of adsorption of SO<sub>2</sub> on different configurations and types of surface alloys as a function of our weighted d-band center. The letters next to each point designate the surface atom or atoms that have been substituted. In Figure 2a,b, Pd–Pt and Cu–Pt alloys, one can discern three different linear relationships. The dot-dashed lines represent the effect of different configurations of the same concentration and type of surface alloy. The dotted lines and the solid lines represent the effect of changing the concentration of alloyed species and show that this effect is linearly additive. Note that the properties of Pd–Pt and Cu–Pt are quantitatively different. These results are somewhat remarkable in that they show that given four carefully chosen points, all of the other points can be estimated to a high degree of accuracy. In particular, the configuration with the highest energy of adsorption and that with the lowest energy of adsorption can be determined.

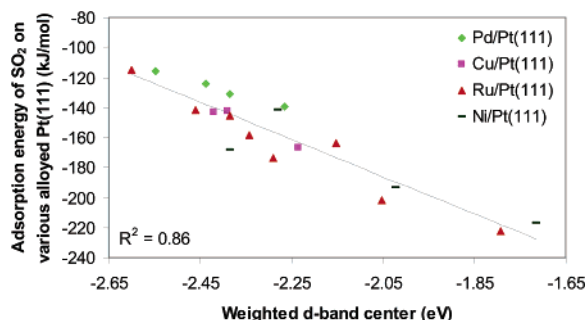
The plot for the Ru–Pt system in Figure 2c, looks different from the other two. Substitution of Pt for Ru on the surface does not lead to additive changes in the energy of adsorption as it does for the Pd–Pt and Cu–Pt systems. All the points fall more or less around the linear solid line in Figure 2c. The trend is that the more substitution of Pt surface atoms by Ru, the higher is the energy of adsorption. Note that substituting Pt for Ru at site b has almost no effect except when b is the last site to be substituted. In the correlations shown here, the term for b in eq 1 is removed.

To show the importance of the  $S^{M-i}$  term in eq 1, the weighted d-band center of various surfaces calculated by our model are compared to those calculated by Pallassana et al.'s model<sup>6</sup> in Table 1. In each series, the binding energy differences between  $x = a/d$  and c, ab and bc, ac and ad, abd and abc could not be captured by Pallassana et al.'s model. This deficiency is clearly illustrated in Figure 2a' by taking Pd/Pt(111) series as an example. Shown in Figure 2a', lines a/d-c, ad-ac-b, acd-ab-bc, and abd-abc/bcd are all perpendicular to the  $x$  axis, which means that Pallassana model cannot distinguish differences within those series. Its application would lead to a qualitatively wrong prediction. The behavior of Pallassana et al.'s model will become even worse in other adsorption systems such as, NO and NO<sub>2</sub> on alloyed Pt(111) surface, which is currently being studied in our group. This is because different surface metal atoms interact with different atoms in the adsorbates. Therefore, incorporating the effects of the type of bond formed between the adsorbate and substrate is necessary for accurately predicting the strength of adsorption.



**Figure 3.** Local d-projected density of state (pDOS) of different atoms of various alloyed surfaces: (a) Pd alloyed Pt(111) surface; (b) Cu alloyed Pt(111) surface; (c) Ru alloyed Pt(111) surface. (Energy values in the legend are the d-band centers for each metal surface atom described by that legend.)

The difference between the Ru–Pt alloys and the other two can be explained by the difference in the local d-projected density of states (pDOS) of the surface atoms. Figure 3a–c illustrate the pDOS of d-orbitals for the surface metal atoms in which the fraction of the alloyed atom is  $1/2$ . The pDOS for the Pt atom in the pure Pt system is also plotted in each figure for comparison. The basic features of the DOS for the surface Pt atoms in each system are similar, but the shapes of the DOS for alloyed atoms (M) in each system are very different. (Refer to the dashed lines in Figure 3.) Even so, the d-band center of Pd in Pd–Pt and that of Cu in Cu–Pt are at almost the same position,  $\sim -2.1$  eV, which is much lower than that of Ru in Ru–Pt,  $\sim -1.8$  eV. It can be seen in Figure 3 that the DOS of Pt atoms in Pd–Pt does not differ very much from that in the pure Pt system. However, compared to the pure Pt system, the DOS of Pt atoms in Cu–Pt shifts slightly toward the Fermi level, whereas that in Ru–Pt shifts in the opposite direction. In addition, the difference in the weighted d-band centers between Pd or Cu and Pt is much smaller than that between Ru and Pt in Ru–Pt. In eq 1, changes in the  $E_d^M$  terms have more effect on  $E_{d\text{-weighted}}$  in  $n$ Ru<sup>x</sup>/Pt(111) systems than in  $n$ Pd<sup>x</sup>/Pt(111) and  $n$ Cu<sup>x</sup>/Pt(111) systems in which changes in the  $S^{M-i}$  terms can have more of an effect. Thus, the effect of alloying each site of the Pt(111) surface on the adsorption energy of SO<sub>2</sub> is more significant with Ru than with Pd or Cu. The higher the surface concentration of Ru, the more significant the difference will be. Other possible reasons to account for the difference between the Ru–Pt alloys and Pd–Pt or Cu–Pt alloys are: (1) the Pt–Ru bond was shown to be stronger than the Pt–Pt bond by about 1.5 eV;<sup>23</sup> therefore the ability for adsorbing the adsorbates after replacing that site with Ru atom will be affected according



**Figure 4.** Linear relationship between stable  $\text{SO}_2$  adsorption on various alloyed Pt(111) surfaces and overlayers vs. the weighted d-band center of the surfaces.

to the bond energy conservation concept; (2) crystal structures of Pd, Cu and Pt are all face centered cubics (fcc) whereas the crystal structure of Ru is hexagonal close-packed (hcp).

The adsorption energies of the most stable configurations of  $\text{SO}_2$  on each system studied (pure Pt(111),  $1\text{Pd}^b/\text{Pt}(111)$ ,  $1\text{Pd}^c/\text{Pt}(111)$ ,  $2\text{Pd}^{bc}/\text{Pt}(111)$ ,  $1\text{Cu}^{b/c}/\text{Pt}(111)$ ,  $2\text{Cu}^{bc}/\text{Pt}(111)$ , and all  $n\text{Ru}^x/\text{Pt}(111)$ ) are plotted in Figure 4 as a function of the weighted d-band centers. Here we define the most stable configurations as those for which the energy of adsorption decreases as sites are substituted one at a time. Figure 4 shows that there is a strong correlation between the adsorption energy of the most stable configuration of  $\text{SO}_2$  and the weighted d-band centers for the surfaces calculated here. Several points ( $1\text{Ni}^b/\text{Pt}(111)$ ,  $1\text{Ni}^c/\text{Pt}(111)$ ,  $2\text{Ni}^{bc}/\text{Pt}(111)$ , and  $3\text{Ni}^{abc}/\text{Pt}(111)$ ) for the  $n\text{Ni}^x/\text{Pt}(111)$  system are included in Figure 4 to test the generality of the linear relationship. The  $R^2$  of the least-squares fitted line in Figure 4 is 0.86, which is as well as the performance of simpler d-band weightings for simpler adsorbates.<sup>2,6</sup> Among the most stable configurations, the farther the weighted d-band center is shifted toward the Fermi energy, the stronger is the interaction of  $\text{SO}_2$  with the surfaces. This is in agreement with observations in the literature for simpler adsorbates, using simpler d-band weightings.<sup>4,6</sup> Applying our model to other systems such as, NO and  $\text{NO}_2$ , shows that our model can be generally applicable.

## Conclusions

We conclude that our approach can model the relative stability of adsorbates on various surfaces, assuming that the adsorbate

adopts the same local configuration on each surface. The types, local concentrations, and the arrangements of the surface atoms can vary. We found that using a new weighting that we have developed, the most stable molecular adsorption strength depends linearly on the weighted position of the d states of the surface relative to the Fermi level. The closer the weighted d-band center to Fermi level, the stronger the adsorption is. Our approach should be useful in general to decide which type and local concentration of surface atoms to choose for designed alloy catalysts.

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