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## Work function investigations of alkali-coadsorbate systems

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**Abstract.** We have measured the work function changes induced by the coadsorption of oxygen or carbon monoxide with sodium as a function of alkali precoverage for the systems  $O_2/Na/Cu(111)$ ,  $O_2/Na/Ni(111)$ ,  $O_2/Na/Cu(110)$ , and  $CO/Na/Ni(111)$ . In agreement with results for many other related systems, we observe anomalous work function decreases for initial doses of both  $O_2$  and  $CO$  for high alkali precoverages. Our results are inconsistent with the standard explanations. We propose a new model in which the work function changes can be accounted for by a competition between two elements: a work function increase due to the coadsorbate and a decrease due to coadsorbate-induced undepolarization of the alkali overlayer.

### 1. Introduction

The coadsorption of oxygen with alkali atoms on both metal and semiconductor surfaces has been studied quite extensively over the past few years [1]. One very interesting experimental observation regarding these systems which has been reported for a number of cases is the qualitative switch in work function behaviour due to the coadsorption of oxygen for low versus high alkali coverages [1–24]. For low alkali coverages below the work function minimum, the addition of oxygen results in an initial work function *increase*, followed by saturation of the work function change at higher oxygen doses. This is similar to the work function behaviour for oxygen dosed onto most bare metal surfaces. In contrast, for high alkali coverages above the work function minimum, the addition of oxygen causes an initial work function *decrease*, with a minimum followed by a rise, and eventual saturation.

This behaviour appears to be quite universal for all metal and semiconductor substrates [1–24]. A number of explanations have been offered to account for these results. The most common are the following:

(i) These changes are related to a transition from ionic to metallic behaviour in the alkali overlayer (before the oxygen is added) [11–13, 18–22], as is often believed to occur at the work function minimum.

(ii) For high alkali precoverages (only), the oxygen initially adsorbs dissociatively underneath the alkali layer [1, 3, 4, 11, 14, 15, 17, 20, 23, 24].

(iii) A different alkali suboxide or oxygen oxidation state is formed for high alkali coverages and low oxygen doses [1–3, 6, 7, 9, 10].

In a previous publication [25] we have presented work function measurements for several systems ( $O_2/Na/Cu(111)$ ,  $O_2/Na/Ni(111)$ , and  $CO/Na/Ni(111)$ ) and have proposed a new model for these and other results which includes as an important component a coadsorbate-induced undepolarization of the alkali overlayer. In this paper we will discuss further these earlier results and our proposed model for work function changes, and present new work function measurements for the system  $O_2/Na/Cu(110)$ , which shows both similarities to and differences from the other systems we have studied.

In section 2 we will briefly discuss the experimental procedures. Sections 3 and 4 contain our experimental results and a discussion of our work function model, respectively. Conclusions will be presented in section 5.

## 2. Experimental details

The work reported here was performed either at the University of Rhode Island or at beamline U14B of the National Synchrotron Light Source, Brookhaven National Laboratory. The Cu(111), Cu(110), and Ni(111) crystals were mounted in UHV systems with standard surface preparation and characterization equipment, and were cleaned by sputtering and annealing cycles. Surface cleanliness was monitored by Auger and/or core level photoemission spectroscopy. The Na was deposited from a thoroughly outgassed SAES getter source equipped with a shutter and collimator, with a pressure rise of  $< 5 \times 10^{-10}$  Torr, from a base pressure in the low  $10^{-10}$  to mid  $10^{-11}$  Torr range. In each case the crystal was clamped to tungsten wires for resistive heating, and the temperature was monitored by a thermocouple attached to the crystal. All evaporations, dosing, and measurements reported here were performed at room temperature. The work function measurements reported here were performed by measuring with a double-pass cylindrical mirror analyser (CMA) the secondary cut-off of photoelectrons ejected by 70 eV incident radiation from the synchrotron.

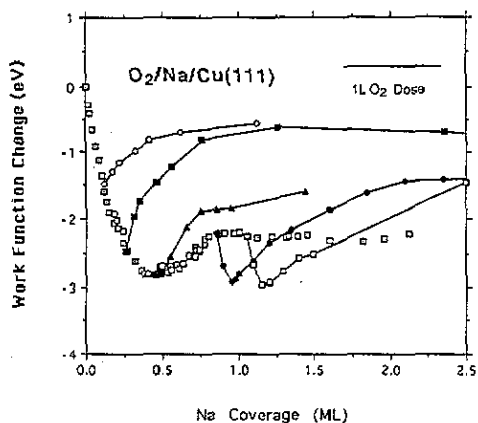
## 3. Experimental results

### 3.1. Coadsorption on the Cu(111) or Ni(111) surfaces

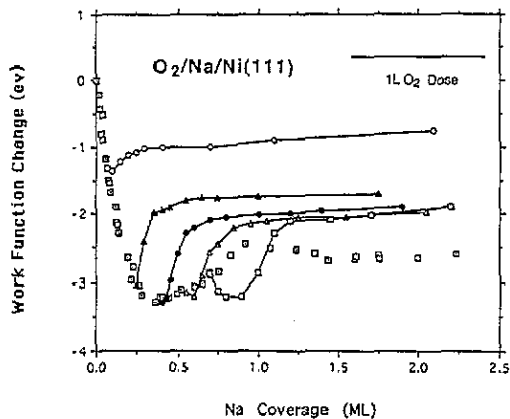
Our work function measurements of  $O_2/Na/Cu(111)$ ,  $O_2/Na/Ni(111)$ , and  $CO/Na/Ni(111)$ , which have already appeared in a previous publication [25], are presented in figures 1–3, respectively. In all three cases, the work function behaviour is quite similar. For low Na precoverages corresponding to coverages below the work function minimum, the work function increases monotonically to saturation as a function of increasing  $O_2$  or CO dose. In contrast, for high Na precoverages, we observed an initial *decrease* in the work function upon coadsorption, followed by a minimum and a subsequent increase to saturation as the dose of  $O_2$  or CO was further increased.

Our results are remarkably similar to most or all previously published measurements for  $O_2$ -alkali [1–24] or CO-alkali [26–32] coadsorbed systems. We have previously argued [25] that these similarities between systems, in particular the qualitatively similar work function behaviour we observed with  $O_2$  or CO coadsorption in the same alkali system ( $Na/Ni(111)$ ), indicate that the mechanism for the anomalous switching behaviour at the alkali work function minimum and subsequent initial decrease must be quite general and virtually adsorbate independent. Specifically, previous models proposed to explain the oxygen results which involve either oxygen incorporation underneath the alkali overlayer or the appearance of different oxygen suboxides are not general enough to account for the CO data as well. (We are not suggesting that our results and interpretation of work function measurements rule out all of the above models for oxygen-alkali bonding, for which there is additional evidence based on other techniques [10, 33, 34], but only question their relevance to work function changes.)

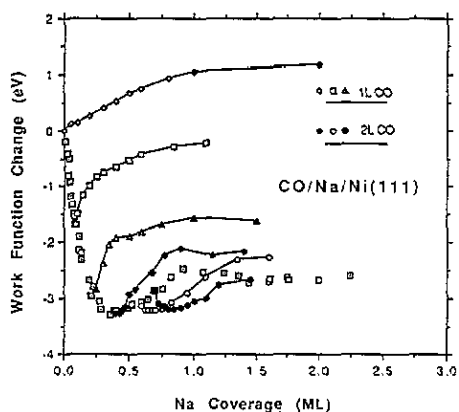
In addition, we have pointed out the persistence of a LEED ring pattern for  $Na/Cu(111)$  [35] and  $Na/Ni(111)$  [36] to high coverages *well past the work function minimum*. This pattern is consistent with alkali-alkali repulsion, which indicates non-metallic behaviour in the overlayer across this coverage range. Together with other



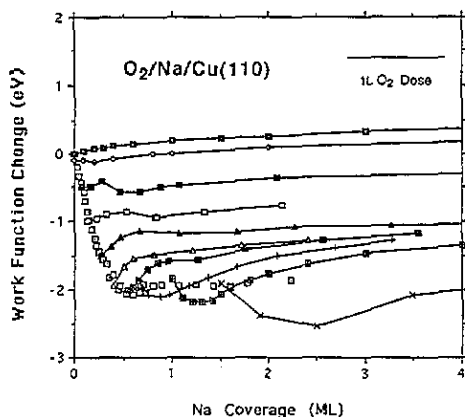
**Figure 1.** Work function change of  $O_2/Na/Cu(111)$  as a function of  $O_2$  dose for various Na precoverages.  $\square$  represents the work function change due to  $Na/Cu(111)$  without any coadsorbate present.  $\circ$ ,  $\blacksquare$ ,  $\blacktriangle$ ,  $\triangle$  represent the additional changes due to the coadsorption with  $O_2$  for different Na precoverages.



**Figure 2.** Work function change of  $O_2/Na/Ni(111)$  as a function of  $O_2$  dose for various Na precoverages.  $\square$  represents the work function change due to  $Na/Ni(111)$  without any coadsorbate present.  $\circ$ ,  $\blacktriangle$ ,  $\triangle$ ,  $\square$  represent the additional changes due to the coadsorption with  $O_2$  for different Na precoverages.



**Figure 3.** Work function change of  $CO/Na/Ni(111)$  as a function of CO dose for various Na precoverages.  $\square$  represents the work function change due to  $Na/Ni(111)$  without any coadsorbate present.  $\diamond$ ,  $\square$ ,  $\triangle$ ,  $\blacklozenge$ ,  $\circ$ ,  $\bullet$  represent the additional changes due to the coadsorption with CO for different Na precoverages. Note the two different CO exposure scales.



**Figure 4.** Work function change of  $O_2/Na/Cu(110)$  as a function of  $O_2$  dose for various Na precoverages.  $\square$  represents the work function change due to  $Na/Cu(110)$  without any coadsorbate present.  $\square$ ,  $\diamond$ ,  $\blacksquare$ ,  $\square$ ,  $\blacktriangle$ ,  $\triangle$ ,  $\boxtimes$ ,  $+$ ,  $\boxplus$ ,  $\times$  represent the additional changes due to the coadsorption with  $O_2$  for different Na precoverages.

measurements of these systems [39], these results suggest that any transition in the nature of the alkali occurs not at the work function minimum for these particular systems, but at a significantly higher coverage. Therefore, explanations for anomalous work function behaviour upon coadsorption resulting from a change in the nature of the alkali overlayer at the work function minimum also cannot be correct in general.

These observations have led us to propose a new model to account for the work function results which we have presented previously [25], and which will be discussed in more detail in the next section. Here we would like to summarize the distinctive features of the work function changes we have observed, as illustrated in figures 1–3, which may be significant

in developing a better understanding of these results and which are important in placing constraints on the model discussed below.

(i) In all cases, the alkali/substrate work function minimum is a turning point between qualitatively different behaviour for low versus high alkali precoverages as a function of coadsorbate dose. In fact, we observed a small initial levelling of the work function change at the minimum for both  $O_2/Na/Cu(111)$  and  $CO/Na/Ni(111)$ , which is discernible in figures 1 and 3.

(ii) For alkali precoverages between the minimum and the completion of the first alkali layer, the second minimum in the work function change (induced by the addition of the coadsorbate) is fairly constant in energy, i.e. independent of alkali coverage.

(iii) For high alkali precoverages, the saturation value for the work function change with coadsorbate dose also appears to be fairly constant in energy independent of alkali coverage, and is slightly above the value for the saturated value of the alkali on the bare metal surface. Our data for high coadsorbate doses are not comprehensive enough to be as certain about this observation, however.

(iv) For low alkali precoverages below the work function minimum, the net increase in work function due to the addition of the coadsorbate increases with increasing alkali coverage, and can exceed, at least for the oxygen systems, the corresponding work function increase due to the addition of the coadsorbate on the bare surface.

(v) For low precoverages of Na, in some cases the coadsorbate-induced work function change appears to increase more rapidly at first, then more slowly, with a change in slope occurring after an exposure of a few tenths of a Langmuir.

(vi) We have already emphasized the significance of the similarities in terms of work function changes between  $O_2$  and CO coadsorption. It should be pointed out that this could be explained simply if the CO dissociates to some extent on the alkali-precovered surfaces. We do not feel, however, based on the results of many other studies of promoted systems, that there is evidence of sufficient dissociation (if any) in these systems to account for these results, though our own measurements cannot eliminate this possibility.

### 3.2. Measurements of $O_2/Na/Cu(110)$

We have recently completed work function measurements of the system  $O_2/Na/Cu(110)$ , and the results are presented in figure 4. This is an interesting system because both oxygen and alkalis separately induce (different) reconstructions of the clean surface [36–39], which may affect the work function results as well. As can be seen by a comparison of figure 4 to our previous measurements of other systems, the qualitative features of  $O_2/Na/Cu(110)$  are in general quite similar. An anomalous initial decrease in the work function is still observed for high Na precoverages, with the Na-induced minimum being a turning point in the behaviour. In addition, the high coverage minimum occurs at approximately the same energy independent of Na precoverage; and the saturation value for high Na coverages appears to be fairly constant. Below the Na-induced minimum, the work function increase due to the addition of  $O_2$  saturates at a higher value for higher Na coverages, and eventually exceeds the magnitude of the increase on the bare surface.

One distinctive difference we have observed for this system compared with our previous investigations, is the occurrence of a shallow minimum in the work function change versus  $O_2$  dose for *low* alkali precoverages. This minimum point corresponds to a decrease of  $\approx 0.05$ – $0.15$  eV depending on the sodium coverage, shifts to higher oxygen dose as the Na precoverage is increased, and disappears before the Na-induced minimum is reached. We believe that these results may be related to structural changes in the Cu(110) substrate, but

further investigation will be necessary to address this issue with more confidence. We will not yet attempt to include this additional complication in our work function model.

#### 4. Work function model

In a previous publication [25] we proposed a new model which can better account for the work function behaviour of the systems discussed above. This model is quite general compared to previous suggestions, and can explain qualitatively and at least semi-quantitatively the similar behaviour for O<sub>2</sub>-alkali and CO-alkali coadsorption (and perhaps other adsorbate-alkali combinations as well). In this model, the coadsorbate-induced work function is assumed to have two separate components: first, CO and O<sub>2</sub> adsorbed on bare metal surfaces both bond in such a way that the work function increases by  $\simeq 1$  eV to saturation for most systems [4, 5, 9, 12, 23, 25-28, 40] (an exception is adsorption on most copper surfaces, for which the work function changes are generally smaller [24, 41, 42]). Second, the interaction between the coadsorbate and the alkali atoms will modify the dipole moments of the alkali atoms which are responsible for the large work function changes on the alkali-covered surfaces without coadsorbates. This effect competes against the work function increase due to the coadsorbate; the net result will depend on both the alkali precoverage and the coadsorbate dose.

In our model, therefore, we express the net work function change,  $\Delta\phi$ , in two parts:

$$\Delta\phi = \Delta\phi_{\text{Coad}} + \Delta\phi_{\text{Undp}} \quad (1)$$

where  $\Delta\phi_{\text{Coad}}$  is the work function change due to the coadsorbate, and  $\Delta\phi_{\text{Undp}}$  is the work function change due to the alkali layer. The latter incorporates the change due to the effect of the coadsorbate on the alkali, which we call 'depolarization'.

The work function change due to any overlayer, can be written in the following general form [43, 44]:

$$\Delta\phi = D(\theta)\theta\sigma_{\text{ML}}/\epsilon_0 \quad (2)$$

where  $D(\theta)$  is the (coverage-dependent) dipole moment per adsorbate in units of Debye (Db) ( $= 0.3333 \times 10^{-27}$  Cb cm),  $\theta$  is the coverage in monolayers, with  $\theta = 1$  defined as saturation of the first layer;  $\sigma_{\text{ML}}$  is the adsorbate monolayer density (which, is, for example,  $8.2 \times 10^{14}$  atoms  $\text{cm}^{-2}$  for Na/Ni(111) at saturation—a coverage corresponding to a surface density  $\simeq 0.44$  times the atomic density of the bare Ni(111) surface); and  $\epsilon_0$  is the free space dielectric, or permittivity, constant ( $= 2.655 \times 10^{14}$  Db  $\text{V}^{-1} \text{cm}^{-2}$ ).

We model the first term in (1) the coadsorbate term, with the following functional form:

$$\Delta\phi_{\text{Coad}} = D(0)_{\text{Coad}} \theta_{\text{Coad}} \sigma_{\text{ML-Coad}}/\epsilon_0. \quad (3)$$

We assume a saturation coverage of 0.5 monolayers for O<sub>2</sub> or CO (typical values for this are in the range of 0.3-0.8 [26-28, 40, 45]), which makes  $\sigma_{\text{ML-Coad}} = 9.35 \times 10^{14}$  atoms  $\text{cm}^{-2}$  for O<sub>2</sub>, CO/Ni(111); we assume that the dipole moment per coadsorbate,  $D(0)_{\text{Coad}}$ , is coverage independent; and we model the coverage term versus coadsorbate dose with  $\theta_{\text{Coad}} = \tanh(BX)$ , where  $X$  is the coadsorbate exposure in Langmuirs. This expression describes a monotonically increasing function which saturates after a coadsorbate dose in Langmuirs of  $\simeq 2/B$ . We adjust the parameters  $D(0)_{\text{Coad}}$  and  $B$ , and found our best fits for values of  $D(0)_{\text{Coad}} \simeq 0.5$  Db and  $B \simeq 1.0 \text{ L}^{-1}$ . We would like to point out that a more detailed analysis of any particular system would require more accurate knowledge and inclusion of absolute coverages as well as the possibility of a coverage-dependent sticking coefficient for the coadsorbate.

In order to describe the coadsorbate-induced undepolarization of the alkali layer, we must first model the work function change due to the alkali (Na in this case) without coadsorbate,  $\Delta\phi_{\text{Na}}$ , with the expression in (2) above. We found that we could fit the experimental data of Na/Ni(111) in the first layer quite well, as displayed in figure 5, with the following form for  $D(\theta)_{\text{Na}}$  (in units of  $D_b$ ):

$$D(\theta)_{\text{Na}} = -((5.10)\theta^2 - (10.97)\theta + 6.78) \quad (\theta \leq 1). \quad (4)$$

The reason for choosing this particular polynomial function will be discussed elsewhere [46], but we would like to emphasize that this functional form is in qualitative agreement with the results of a first principles calculation of the dipole moment of Na/jellium by Ishida [47].

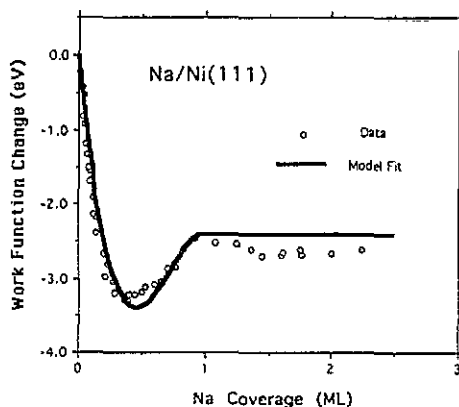


Figure 5. Measurements and a model fit to the work function change of Na/Ni(111) as a function of Na coverage.  $\theta$  is defined as the density corresponding to saturation of the first Na layer.

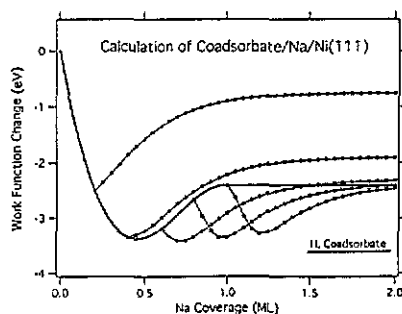


Figure 6. Model calculation for the work function change of alkali plus coadsorbate as a function of coadsorbate dose for various alkali precoverages. The work function curve for the alkali without coadsorbate is a best fit to our data for Na/Ni(111). (Version 1 of the model, see text for details.)

When a coadsorbate such as  $\text{O}_2$  or  $\text{CO}$  is added to the alkali overlayer at some particular alkali coverage,  $\theta$ , the two species will interact in a mainly short-range manner [48]. We suggest that, in terms of work function changes, this interaction can be adequately described by assuming that the coadsorbate atom locally ties up one or two neighbouring alkali atoms, thus removing them from the dipole array that determines the dipole moment per atom,  $D(\theta)_{\text{Na}}$ . In our model, we remove the affected alkali atoms from this array by replacing the actual alkali coverage,  $\theta$ , in (4) with an effective coverage,  $\theta_{\text{eff}}$ , which is less than the actual coverage. The effect of the coadsorbate on the alkali part of the work function is thus given by the following relation:

$$\Delta\phi_{\text{Undp}} = D(\theta_{\text{eff}})_{\text{Na}}\theta\sigma_{\text{ML}}/\epsilon_0. \quad (5)$$

We have chosen still to count all of the alkali atoms while assigning them a dipole moment modified by the coadsorbate-induced effective coverage. A preliminary analysis with  $\theta_{\text{eff}}$  substituted for  $\theta$  in (5) did not cause significant changes in the results.

We have modelled the effective alkali coverage as follows:

$$\theta_{\text{eff}} = \theta[1 - C\theta \tanh(DX)] \quad (6)$$

where  $C$  and  $D$  are adjustable parameters, with best fits in the range of  $C \simeq 0.3$  and  $D \simeq 4 \text{ L}^{-1}$ . The  $\tanh$  term causes this quantity to saturate at higher coadsorbate exposures,

which is consistent with evidence that the primary alkali-coadsorbate interaction is short-range [48]. The adjustable parameter  $C$  determines the saturation value of the effective coverage. To achieve reasonable agreement with our data, we found it was necessary to include the  $\theta$  factor in the brackets as well. This increases the depolarization effect for high alkali precoverages, which is somewhat reasonable since more atoms are available for bonding; the density is also higher so more than one alkali atom could be affected by the addition of a coadsorbate atom or molecule. In addition, this term also tends to compensate for the increase in coadsorbate sticking coefficient which has been detected for higher alkali precoverages in some systems [1, 22].

*Version 1.* The result of our first attempt at fitting our work function data (concentrating on the  $O_2/Na/Ni(111)$  system, though all systems are quite similar), was presented in a previous publication and is reproduced in figure 6. For this model we used the following values of the adjustable parameters:  $D(0)_{\text{Coad}} = 0.511$  Db,  $B = 1.0$  L<sup>-1</sup>,  $C = 0.3$ , and  $D = 4.0$  L<sup>-1</sup>. Clearly we have been able to produce many of the significant qualitative features of the work function changes of these systems. Most important, the coadsorbate-induced work function behaviour goes through a transition at, or very close to, the alkali-induced work function minimum in good agreement with all of our measurements. In addition, this model with these parameters also produced work function changes for high alkali precoverages for which the values at the secondary minima and at saturation are approximately alkali coverage independent.

*Version 2.* A second version of our model, which is presented here for the first time, was motivated primarily by the fact that, firstly, to obtain the results presented in figure 6 we needed to impose rather large work function changes on the coadsorbate without alkali. The choice of  $D(0)_{\text{Coad}} = 0.511$  Db translates into a 1.8 eV upward shift for the coadsorbate on the bare surface (not shown in figure 6), somewhat larger than is usually obtained experimentally. Secondly, version 1 produces net increases for low alkali precoverages which become smaller with increasing coverage, contrary to observations. In addition, as discussed above, there is some evidence for a break in the slope of the work function change at low alkali and coadsorbate coverages (see figures 2 and 3, in particular).

This break point at low coverages suggests the importance of considering again the primarily short-range nature of the coadsorbate-alkali interaction; the evidence for this has been documented particularly for CO coadsorption [48]. For low alkali precoverages, only the first coadsorbate atoms adsorbed will interact strongly with the alkali. In version 1, we already saturated the  $\Delta\phi_{\text{Undp}}$  term by including the  $\tanh(D)$  function (6). In this second version of the model we divide the  $\Delta\phi_{\text{Coad}}$  term into two ranges to reflect the short-range interaction of the coadsorbates with the alkalis. The total work function change is now written as:

$$\Delta\phi = \Delta\phi_{\text{Coad}_{1,2}} + \Delta\phi_{\text{Undp}} \quad (7)$$

with  $\Delta\phi_{\text{Undp}}$  given as above in (5) and (6) and  $\Delta\phi_{\text{Coad}_{1,2}}$  given as follows:

$$\Delta\phi_{\text{Coad}_{1,2}} = \begin{cases} D(0)_{\text{Coad}-1} \tanh(BX) \sigma_{\text{ML-Coad}} / \epsilon_0 & \text{for } X(L) \leq 2\theta_{\text{Na}} \\ D(0)_{\text{Coad}-2} \tanh(BX) \sigma_{\text{ML-Coad}} / \epsilon_0 & \text{for } X(L) > 2\theta_{\text{Na}} \end{cases} \quad (8)$$

The results of the best fit to our data with this version of our model are displayed in figure 7. The values of the parameters used to produce these curves are  $D(0)_{\text{Coad}-1} = 0.57$  Db,  $D(0)_{\text{Coad}-2} = 0.213$  Db,  $B = 1.0$  L<sup>-1</sup>,  $C = 0.325$ , and  $D = 4.0$  L<sup>-1</sup>.

This model calculation, containing what we think is a reasonable selection of parameters, can successfully reproduce all of the significant features of our work function measurements as summarized in section 3. One additional comparison we can make to experimental



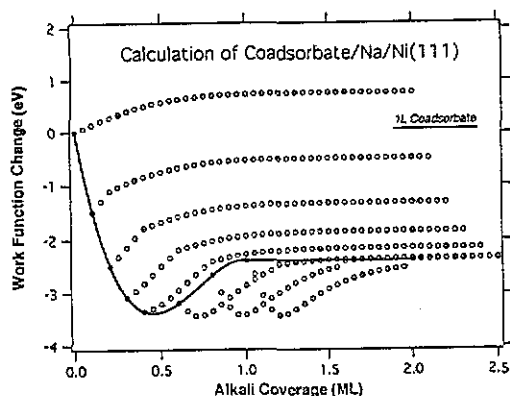


Figure 7. Model calculation for the work function change of alkali plus coadsorbate as a function of coadsorbate dose for various alkali precoverages. The work function curve for the alkali without coadsorbate is a best fit to our data for Na/Ni(111). (Version 2 of the model, see text for details.)

results is the dipole moment which corresponds to the coadsorbate on the 'bare' parts of the surface,  $D(0)_{\text{Coad}-2}$ . For the surface without alkali, only this term contributes to the work function. As a comparison, we find good agreement of this fitted parameter for the initial dipole moment of the coadsorbate of 0.213 Db with the experimentally determined value for CO/Ni(111) of 0.28 Db by Campuzano *et al* [49]. In addition, they found that the CO dipole moment was coverage independent (up to a saturation coverage of  $\approx 0.57$ , close to the value of 0.5 used in this model), which is the assumption we have made for the coadsorbate term in both versions of our model.

The incorporation of a second type of coadsorbate with a relatively high dipole moment, implies that due to the interaction with the alkali atoms, the dipole moment associated with the initially adsorbed coadsorbates in the presence of the alkali is larger than for the same coadsorbates on the bare surface. It may be possible to correlate this to measurements of local work function changes with the PAX technique [50]. It should be noted that a range of values near the parameters given above also give similar and satisfactory results. It is not clear if any further insight will be gained at this level of the model by more carefully determining 'acceptable' parameter sets. Again, absolute coverages and correct sticking coefficients also need to be taken into account to push this model any further or apply it to any particular system.

We would now like to summarize the important features of our work function model (version 2, in particular): when the alkali coverage is low, the addition of a coadsorbate results in only a relatively weak undepolarization effect on the alkali atoms themselves. The work function change is dominated by the dipole moment of the coadsorbate, which is modified through the short-range interaction with the alkali atoms. As the coadsorbate coverage increases, the alkali atoms are 'used up', and the remaining work function change is caused by the adsorption of the coadsorbate on the bare and unperturbed portions of the surface.

For high alkali coverages, the strong depolarization effect has already caused the alkali-induced work function to pass through a minimum and increase. The subsequent addition of the coadsorbate has a greater effect on this depolarization, disrupting the alkali-alkali interactions through the strong short-range alkali-coadsorbate bond. The undepolarization of the alkali layer by the coadsorbate reduces the work function approximately back to the previous minimum value. With further increases in coadsorbate coverage, the main undepolarization effect is somewhat saturated and the work function increases again due to the (alkali-modified) dipole moment of the coadsorbate.

The model described above was primarily intended to describe the work function changes for submonolayer coverages of alkali-coadsorbate systems, but it may also be

applicable for thicker alkali layers, for which oxygen-induced work function decreases have also been observed [10, 51]. The multilayer case can become more complicated since there is the likelihood of forming three-dimensional alkali oxide compounds [51]. Nevertheless, it is interesting to note that in a study of O/K/Ru(001) by Rocker *et al* [10], the addition of oxygen to a three layer potassium film caused the work function to decrease to the value at the submonolayer K-induced minimum, very similar to our observations for submonolayer coverages of sodium plus oxygen or carbon monoxide on copper and nickel surfaces.

We would also like to point out some similar features of the present model to a previous calculation of coadsorbed systems by Albano [52]. He considered the dipole-dipole interactions between the alkali and coadsorbate and was able to reproduce experimental results for a couple of systems. The main difference between this model and our model is that Albano considered only the long-range interactions of the alkali and coadsorbate, while we have concentrated on the importance of short-range interactions. It is possible that both may contribute to different degrees in a complete analysis of these systems.

## 5. Conclusions

We have measured the work function changes induced by the coadsorption of oxygen or carbon monoxide with sodium as a function of alkali precoverage for the systems O<sub>2</sub>/Na/Cu(111), O<sub>2</sub>/Na/Ni(111), CO/Na/Ni(111), and O<sub>2</sub>/Na/Cu(110). We observed anomalous work function decreases for initial doses of both O<sub>2</sub> and CO for high alkali precoverages as well as other features which are system independent. Our data are inconsistent with the standard explanations for these results. We propose a new model in which the work function changes induced by the coadsorbate involve a combination of work function increase due to the coadsorbate dipole moment and work function decrease due to coadsorbate-induced depolarization of the alkali overlayer.

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