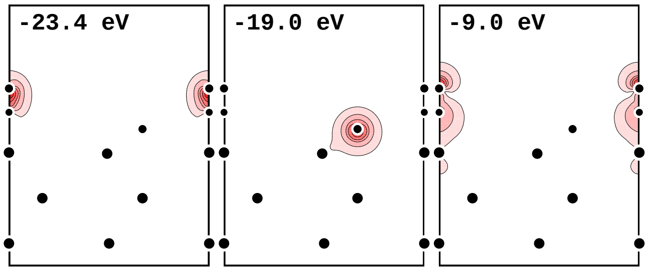


Figure 3.102: The orbital density of the deepest Kohn-Sham states in the structure Ru (0001)-(2 × 2)-($CO_{ot}$+$O_{hcp}$)

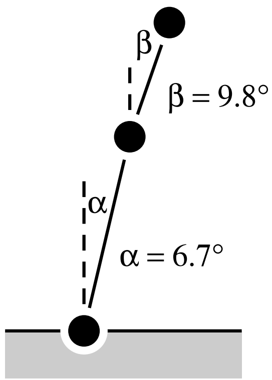


Figure 3.103: The final tilted geometry of the structure Ru (0001)-(2 × 2)-($CO_{ot}$+$O_{hcp}$) when the lateral coordinates were allowed to relax

and we started from somewhat a larger tilt angle in order to diagnose whether the tilt would reduce to the experimental one. However, the final geometry, where the forces on the atoms were zeroed, in the Figure 3.103 shows a smaller tilt, 7.9°, but the main problem is the energetics: most likely due to the discretisation errors, discussed in the Section A.3, the energy at the up-right geometry is some 20 meV lower than in the tilted one, yet the atoms of the CO molecule did not relax to this geometry when let to move freely. Thus either there is a meta-stable minimum at the tilt angle 7.9° in our calculations or it is due to the discretisation errors. In any case the potential energy surface for a tilt is rather flat; more studies would be necessary to clear this issue.

## 3.5 Discussion

Here we shall collect and analyse the main results achieved in the previous Sections and view them from a wider perspective. Especially the trends upon changes in the coverage and co-adsorption will be paid special attention for and whenever possible the accuracy of the calculations is measured against the experiments. References to literature and our unpublished work will be made whenever appropriate.

### 3.5.1 Bulk ruthenium and clean (0001) surface

Ruthenium with its location in the platinium group metals in the Periodic Table has the Fermi level cutting through the 4*d* band and thus an open *d* shell which easily hybridises with more electro-positive or -negative species. The (0001) surface, with the highest atomic density of the hexagonal close packed lattice, is very similar to the (111) surface of the face centred crystal and the difference does not affect the electronic structure appreciably (Ari P Seitsonen, unpublished results). At the surface layer the density of states gets narrower especially for the $d$ states due to the reduced coordination and thus a smaller dispersion; the centre of the band has to raise slightly energetically in order to maintain the charge neutrality, and the most significant different difference in the electronic states to the bulk layers is the last peak of the $d_{z^2}$ states which has lowered itself partially to the Fermi level already. It is these states which are emptied upon the adsorption of *e.g.* nitrogen to the surface (Schwegmann *et al*, 1997). The outer-most layer of the clean surface is found to relax slightly inwards, in agreement with the experiments and the earlier calculations, as response to the reduced coordination of the atoms at the surface layer.

### 3.5.2 Adsorption of single species

The present studies bring a large amount of previously unexplored details of the adsorption of alkali metals into daylight, although we haven't yet even fully understood all of them. Our main concern in these calculations was the use of pseudo potentials to describe the cesium atom since the outer-most 6$s$ state might change considerably during the adsorption also in the core region and would thus invalidate the frozen-core approximation. However include the semi-core states 5$s$ and 5$p$ into the active valence states of the pseudo potential we have achieved, with the exception of the slightly erroneous binding energies, a level of accuracy in comparison to the experiments which has been qualitatively found in the results for the generalised gradient approximation, namely the geometries are generally in agreement with the experiments beyond the over-estimation of the lattice constant, and the magnitude of the change in the work function is underestimated but the qualitative trend is accurately reproduced. Thus we are confident that our results are quantitatively correct within the limits of the generalised gradient approximation and we can access also new information about the applicability of the generalised gradient approximation for the configurations at hand and catalytic systems in general.

The geometries of cesium on the Ru(0001) agree reasonably with the experimental values from the low energy energy diffractive measurements (Over *et al*, 1992b): The cesium-ruthenium layer heights are too small and the buckling is too large; yet the change when going from the $(\sqrt{3}\times\sqrt{3})$R30° to the $(2 \times 2)$ cell is more accurately tracked. It would also be interesting to see the whole effect of a finite temperature on the geometries of our structures since the potential energy surface for the lateral and vibrational movement of the cesium is very shallow. The adsorbed cesium pushes the atoms laterally away from it at the hcp site and vertically on the on-top site – vice versa the changes are negligible – and the magnitude of these changes decreases towards the lower coverages which at first sounds counter-intuitive as at low coverages the adsorbates are further away and thus there would be more atoms of the substrate in between to adjust for the local changes in the geometry around the adsorbates. However the larger changes at the high coverages might be due to a need to electronically screen the remaining dipole-dipole repulsion between the cesium atoms (Over *et al*, 1995a). The distance between the first and second ruthenium layer remains practically constant throughout the range of coverages studied here, but remarkably the height of the cesium from the outer-most substrate layer increases towards the lower coverages when rather a smaller distance would be expected since according to the the dipole moment, and thus also the "ionicity", of the cesium increases and the ionic radius of a cesium atoms is smaller than the covalent one. For the time being this trend remains mysterious and awaits for a confirmation from the experiments;

yet an equivalent behaviour was found from the low energy electron diffraction measurements for several alkali metals on the Ag (111) surface (Kaukasoina *et al*, 1997), potassium on the Ni (100) (Wedler *et al*, 1993) and a similar effect was suggested (Schuster, Eng and Robinson, 1995) for Cs on the Ag (110) surface. The difficulty in reaching these occurrences is due to the low coverages and temperatures, in order to avoid the easy diffusion of the alkali metal atoms, required and then the surface becomes quickly polluted by the residual gases. We further note here that an increase in the distance of the cesium from the surface atoms could explain the unexpected down-ward shift in the Cs-Ru frequency when going to lower coverages (He & Jacobi, 1996).

The main effect caused by the cesium on the electronic structure of the ruthenium substrate is the polarisation and filling of the $d_{z^2}$ orbitals *i.e.* exactly those which were largely abundant just above the Fermi energy at the clean surface. Exactly the same result can be achieved by instead of adsorbing the cesium an electric field is applied parallel to the normal of the surface. In the $(2 \times 2)$-Cs structure we find the magnitude of the vertical component of the electric field at the other high-symmetry sites to be about 1.7 eV/Å and still 1 eV/Å at the site furthest away from the cesium at the coverage of 1/9. The change in the electronic charge density around the cesium is dominated by the counter-polarisation of the 5*s* and 5*p* states against the change in the 6*s* orbitals, and it remains to be seen from all-electron calculations to which extent this effect would be an error due to the use of pseudo potentials. Furthermore the change in the density on the jellium is similar as on the Ru (0001) surface; the adsorption energy is 0.91 eV, half of the adsorption energy on the Ru (0001) surface which can be regarded to be large. The fcc (111) surfaces of rhodium and platinium seem to behave qualitatively in the same manner as the Ru (0001) upon the adsorption of alkalis to them.

In the case of the carbon monoxide we studied coverages from 1/4 to 1 mono-layer, and the adsorption site was always the on-top position although it is known experimentally that at the coverages above 1/3 up to the maximum coverage achieved $\simeq$2/3 the molecules adsorb also at different sites, most likely in compressed over-layers, and the only ordered structures found up to date are the $(\sqrt{3} \times \sqrt{3})$R30°, $(2\sqrt{3} \times 2\sqrt{3})$R30° and $(5\sqrt{3} \times 5\sqrt{3})$R30°; however our results act as a model for the adsorbate-adsorbate interactions. We see the internal carbon-oxygen bond length decreasing towards the values of the free molecule and simultaneously the distance from the nearest-neighbour ruthenium increasing; the change in the work function is similar, although somewhat larger, than in the experiments. The binding energy is attractive at the coverage of 1/3, in agreement with the experiments, where island formation to the $(\sqrt{3} \times \sqrt{3})$R30° is found at lower coverages.

Electronically we find the adsorption mechanism to support the Blyholder model, where the main changes upon a bonding to the surface is via the states $5\sigma$ and $2\pi^*$ as seen from the Figure 3.62. Yet quantitatively the mechanism is closer to the one proposed by Nilsson *et al* (1997) the $4\sigma$ and $1\pi$ taking part to the bonding as well; this effect was already seen in the calculations of Aizawa and Tsuneyuki (1998) but not discussed any further. However we find one more state in addition to the mixed $4\sigma$ and $5\sigma$ states; please see the Kohn-Sham state at $-7.50$ eV in the Figure 3.61. Its magnitude in the densities of states remain small though, or is inherent in the eigenvalues caused by the $5\sigma$ state. The $4\sigma$ forms a strong covalent bond with a *d* state of the substrate. At the Fermi energy the adsorption of the carbon monoxide causes a reduction in the density of states similar to the atomic nitrogen (Schwegmann *et al*, 1997) and opposite to the case of the electro-positive cesium as seen above.

The adsorption at different sites has a definitive consequence on the energetic location of the molecular states of the carbon monoxide agreeing with the conclusions derived by Strisland *et al* (1998) for K+CO/Rh (111); the very small energy difference between the on-top and hcp sites might be a short-coming of the generalised gradient approximation since in the cases of the Pt (111) and Cu (111) the three-fold hollow site is incorrectly to be the stable adsorption site and also at the Rh (111) the corrugation of the potential energy surface is obtained as very small. On at the Pd (111) and Ir (111) the energy difference came out as appreciable; at the former the co-adsorption experiments (Conrad, Ertl & Küppers, 1978; Oed *et al*, 1988) with oxygen can indeed be interpreted as proving a larger corrugation with a preference for the fcc site as discussed by Over (1998).

We have found the $N_2$ to behave much more similarly to the carbon monoxide than what was deduced by de Paola *et al* (1987); the same qualitative difference is present also upon the co-adsorption with cesium (Ari P Seitsonen, unpublished results). We have no explanation for the discrepancy at the time being; yet the electronic states behave beautifully like seen in the experiments by Nilsson *et al* (1997) for $N_2$/Cu (100).

The adsorption of the atomic oxygen onto the Ru (0001) proceeds similarly to the nitrogen (Schwegmann *et al*, 1997) with the exceptions mentioned earlier. However the sulphur, despite the iso-electronic valence with the oxygen, yields a decrease in the work function at high coverages relative to the clean surface (Ari P Seitsonen, unpublished results). The local density approximation gives similar but slightly lower changes in the work function as the generalised gradient approximation in the case of the oxygen; a very similar difference is found also for oxygen on Ru $(10\bar{1}0)$ (Schwegmann *et al*, 1998; Ari P Seitsonen, unpublished results). We notice that in both cases the changes obtained from the local density approximation are very close to the experimental values and since also the values of the clean surfaces are accurate we conclude that in these cases the local density approximation can be used in quantitative comparisons with the experiments and has thus also predictive power. On the contrary the values from the generalised gradient approximation produces too low a work function for the clean surface, by 0.4 eV, and too large changes in the case of cesium, carbon monoxide and oxygen on the Ru (0001) based on the present work, and the over-estimations vary being respectively about 0.6, 0.3 and 0.2 eV; therefore although the changes correct the under-estimation of the value at the clean surface the amount of the correction might not be reliable and thus even the absolute values of work function from the generalised gradient approximation must be used with care.

### 3.5.3 Co-adsorption

Experimentally (Over, 1998) the co-adsorbed cesium and oxygen has been found to possess a rich phase diagram, with structures which can be described already as surface oxides rather than as co-adsorbate phases with the identity of the individual adsorbates. Unfortunately we are still limited to smaller unit cells, but even then there are experiments to compare our results with.

In the structure $(\sqrt{3} \times \sqrt{3})$R30°-(1Cs+1O) the symmetry necessarily decreases, in this case from $C_{3v}$ of the phase $(\sqrt{3} \times \sqrt{3})$R30°-Cs to $C_3$ *i.e.* the mirror plane symmetries are absent. This gives the three ruthenium atoms of the first substrate layer the freedom to rotate by 1.1° around the three-fold rotational axis and the ruthenium atoms move laterally closer to the oxygen atom the the cesium or the third, empty hcp site. This causes the surprisingly large adsorption height of the oxygen of 1.54 Å compared to the height 1.19 Å in the $(2 \times 2)$ or 1.28 Å in the $(\sqrt{3} \times \sqrt{3})$R30° phases of the oxygen alone; this might have an electro-static origin if a small layer height between the cesium and oxygen would be preferred, which however is un-probably since it is not seen in the other phases studied here.

In the phase $(2 \times 2)$-(1Cs+1O) then the oxygen pushes its nearest-neighbour ruthenium atoms away with a lateral magnitude of 0.08 Å and thus the oxygen atoms can get deeper towards the surface, to be compared with 0.09 Å of the isolated phase $(2 \times 2)$-O; in the pure structure $(2 \times 2)$-$Cs_{ot}$ the change is in the same direction as in the co-adsorptive case but is only 0.01 Å. Now that a vertical buckling is possible the ruthenium atom below the cesium is pushed inwards decreasing the cesium-oxygen distance which remains though larger by 0.15 Å than in the $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ phase. The three oxygen atoms in the structure $(2 \times 2)$-(1Cs+3O) force the cesium again to the hcp site, and both the lateral shift and the buckling decrease as the coverage of the layer thus increases. However whereas the agreement to the experiments is good – within the typical accuracy of the generalised gradient approximation – in the previous two phases here the vertical distances match rather poorly, an effect which awaits for an explanation.

Overall the interaction between the cesium and oxygen is of an attractive type as expected from a combination of an electro-positive and -negative species: The hard-sphere radius of the cesium atom is smaller throughout the systems here than in the isolated Cs/Ru phase in agreement with the simple picture of a charge transfer from the cesium to the oxygen and thus a decrease in the effective size of the cesium towards its ionic radius.

The co-adsorption of cesium and carbon monoxide forms an important model for the interaction between the carbon monoxide, or a simple reactant, with the alkali promoter. As in the co-adsorbate system of cesium and oxygen also here the adsorbate pair consists of the electro-positive alkali atom and a particle which can act as an electron acceptor, in this case the carbon monoxide can fill the initially unoccupied $2\pi^*$ orbital, which was already seen to occur at the single-adsorbate phase, according to the Blyholder model. Thus our results can reveal whether, and if yes to what extent, this trend is enhanced upon the co-adsorption of the cesium.

Unfortunately we are currently incapable of studying the co-adsorption as a function of the coverages of both the adsorbates, and thus our chances to learn about the range of the mutual interaction are limited. Yet the carbon monoxide can occupy the otherwise un-preferable fcc site in the structure $(2 \times 2)$-($1Cs_{ot}$+$2CO_{hcp,fcc}$) to increase the CO coverage to 1/2. Based on the occurrence of two separate C-O vibrational frequencies in the high resolution electron energy loss spectra He, Xu and Jacobi (1996) suggested that the phase $(2 \times 2)$-(1Cs+2CO) begins to form already before the $(2 \times 2)$-(1Cs+1CO) phase has been completed; however we obtain the separation of the two islands $(2 \times 2)$-(1Cs+2CO) and $(2 \times 2)$-Cs to be energetically by 0.62 eV compared to the homogeneous layer $(2 \times 2)$-(1Cs+1CO): The repulsion among the cesium atoms in the pure $(2 \times 2)$-Cs structure over-weights the modest energy win of clustering the higher-coverage co-adsorption structure from the CO/Ru-only phase. A possible explanation for the different behaviour from the experiments and our calculations could be that at the inter-mediate coverage the CO molecules are rather immobile and molecules sticking to the $(2 \times 2)$-(1Cs+2CO) islands cannot diffuse to the cells with only $(2 \times 2)$-Cs. Otherwise the attraction between the cesium and carbon monoxide is strongly attractive as expected, with a mutually stabilising effect of nearly 1 eV relative to the isolated phases.

Since both the carbon monoxide and the cesium atom prefer the on-top site in the single-adsorbate phases with the $(2 \times 2)$ registry – although the energetics of the cesium is somewhat erroneous and the corrugation of the potential energy surface for the adsorption of the carbon monoxide under-estimated – in the $(2 \times 2)$ co-adsorbate cell either the symmetry has to be lowered to $C_{1h}$ or at least either one of the adsorbates has to occupy an adsorption site different from its isolated phase, and the latter scenario has been found to take place in the experiments. Although the move of the cesium to a three-fold hollow site would be energetically easier than of the carbon monoxide the structure $(2 \times 2)$-$(1\mathrm{Cs_{ot}}+1\mathrm{CO_{hcp}})$ is much more, by 0.44 eV, more stable than $(2 \times 2)$-$(1\mathrm{Cs_{hcp}}+1\mathrm{CO_{ot}})$; possible explanations would be a preferred electro-static interaction – the oxygen atom of the carbon monoxide is positioned lower in the former structure and thus the increase in the density around the oxygen is located further away from the density increase above the cesium atom – or an easier filling of the $2\pi^*$ orbital of the carbon monoxide as found by Müller (1989) from the cluster calculations for the system K+CO/Pt(111). In both Cs+CO/Ru structures the interaction density is consistent with an enhanced Blyholder mechanism due to a increase in the density at the sides of the CO molecule, where the $2\pi^*$ orbital resides, and a decrease on the molecular axis between and above the atoms nicely correlating with the density of the $5\sigma$ orbital; however the main effect in the stable $(2 \times 2)$-$(1\mathrm{Cs_{ot}}+1\mathrm{CO_{hcp}})$ structure is the internal polarisation of the CO molecule. This change can be accurately reproduced with an electric field perpendicular to the surface as was also the case for the clean surface. The density around the cesium is little changed upon the adsorption of the carbon monoxide.

The change in the density around the cesium by the asymptotic density above the atom; this shows a clear qualitative difference between the structures with co-adsorbed carbon monoxide or oxygen: In the case of the former the asymptotic density is largely depressed and in the latter closer to the phase of $(2 \times 2)$-Cs only; the decrease in the case of the co-adsorbed CO occurs simultaneously with an increase of the height of the cesium layer from the out-most layer of the substrate. The same trend in the induced density arising from the Kohn-Sham states near the Fermi energy a small but definite effect is seen: Whereas the co-adsorption with oxygen increases the density above and close to the surface the carbon monoxide reduces it. The same conclusion was derived from the meta-stable de-excitation spectra of impinging helium and neon atoms by Fichtner-Endruschat *et al* (1998). Thus this gives promise for the applicability of the calculated densities to the interpretation of the experimental spectra.

An effect which has been found already in most of the measurements on the quantitative geometry of the co-adsorption of an alkali atom and the carbon monoxide is the bond lengthening of the internal carbon-oxygen distance in the CO molecule. We have observed the same effect and we can also observe the gradual raise and origin of the effect: The total change from the isolated $(2 \times 2)$-$\mathrm{CO_{ot}}$ to the co-adsorbed $(2 \times 2)$-$(\mathrm{Cs_{ot}}+\mathrm{CO_{hcp}})$ phase amount to 0.10 Å, from which 0.03 Å occurs already upon the change of the adsorption site $\mathrm{CO_{ot}} \Rightarrow \mathrm{CO_{hcp}}$ and further 0.02 Å is achieved by the applied electric field in the absence of the cesium; however we were limited to a magnitude of about one third of the electric field above the hcp site which is created by the cesium, and if we assume a linear dependence of the C-O bond length on the strength of the electric field we obtain a total change of 0.03 Å+3×0.02 Å = 0.09 Å, close to the real value in the co-adsorption structure of 0.10 Å. The increased carbon-oxygen bond distance due to the site change, probably combined with the electric field arising from the alkali atom, accounts for the reduced C-O vibrational frequency seen in the vibrational spectroscopies upon the co-adsorption. The increase in the bond length upon the adsorption of the carbon monoxide and further when the alkali atom is added to the vicinity of the molecule could simply be explained by the increasing filling of the molecular $2\pi^*$ state which is anti-bonding with respect to the internal C-O bond and this way the carbon atom can be bind more strongly to the surface; the increased binding energy of the CO in the presence of the alkali can also be of an electro-static origin. Another scheme to explain the bond lengthening is that first the carbon atom forms the bond to the surface and subsequently the internal C-O bond has to be weakened. Our increase values for “charge” from the projection of the electronic states of the adsorbed system onto the orbitals of the CO molecule support the former scenario. The properties of a free, charged CO molecule behave qualitatively similarly to the adsorbed molecule upon the change caused by a co-adsorbed alkali atom.

According to our results the adsorption site is the most important factor in determining the energy of the peak position of the molecular states of the carbon monoxide, with the single exception in the structure Ru (0001)-$(2 \times 2)$-$(1Cs_{hcp}+1CO_{ot})$ which however is not the stable configuration of this co-adsorption system. In the other cases for example the $3\sigma$ peak varies between $-22.3$ and $-21.8$ eV at the hcp and only between $-23.4$ and $-23.3$ eV at the on-top site; similarly for the $4\sigma$ peak the energies are hcp: $-10.1\ldots-9.6$ eV, on-top: $-9.0\ldots-8.9$ eV. Especially small is the influence of one or even two co-adsorbed oxygen atoms: no peak moves more than 0.1 eV, pointing towards rather a weak interaction. All in all the set of energies of the molecular states are – with the one case violating the rule – a characteristic feature of a deterministic adsorption site and less of the chemical environment of the carbon monoxide. The same conclusion was recently suggested by Strisland *et al* (1998) from photoemission experiments, and the core level spectroscopy often relies on such assignments.

The opposite effect of the co-adsorptive electro-positive cesium and electro-negative oxygen on the carbon monoxide is apparent from several factors: The bond length increases when cesium is co-adsorbed but even decreases in the case of oxygen; as mentioned above the energetic positions of the CO are hardly changed with co-adsorbed oxygen but more with cesium; the cesium decreases, oxygen increases the bond length from the carbon to the nearest-neighbour atoms at the substrate.

A clear indicator of the site determination induced by either the co-adsorbed cesium or oxygen is obtained from the comparison of the two co-adsorption systems K+CO/Ru (0001) and O+CO/Ni (111): Whereas in the former the potassium causes the carbon monoxide to move from the on-top site to the hcp site in the latter the oxygen forces the CO in the opposite direction from the other three-fold hollow fcc site to on-top; so far there has been no counter-example of a change of the adsorption site in the “forbidden” direction (Over, 1998). Thus again the reasoning of the electro-positivity and -negativity of co-adsorbates supports the qualitative out-come of the Blyholder model.

Finally we still remark that large changes in the vertical corrugation – up to 0.24 Å – and lateral shifts – 0.09 Å – have been obtained in the studies of the present work; these are large effects on the chemical length scale and thus imply rather an active interplay of the surface during the adsorption and thus the catalytic processes.