well as the $4\sigma/5\sigma$ mixing. The "charge" at the CO molecule, obtained by summing up the integrals of the projections onto the molecular orbitals, shows a larger value at the hcp site, and as expected at the on-top site the charge decreases – along with an increase of the $4\sigma/5\sigma$ mixing – when the electro-negativity of the co-adsorbate increases. This is mainly due to the increased occupation of the $2\pi^*$ level; such a trend is in accord with the Blyholder model, although the change of the 5σ orbital is minimal. We warn, however, that the "charge" and orbital overlap should be regarded with some caution as the overlap in the adsorbed structure can also include some of the states of the substrate because the orthogonality between the substrate and molecular states does not hold when the hybrids have been formed.

The density of states projected at the atomic orbitals of the cesium atom reveals that the position of the semi-core $5s$ and $5p$ states shifts first upon its adsorption and further when co-adsorbates are added; the carbon monoxide increases the Kohn-Sham eigenvalues more than oxygen, and the more co-adsorbates the larger the increase. As was also seen in the Section 3.3.1 these eigenvalues are almost independent of the adsorption site, which is easily understandable due to the large distance of the cesium from the surface and the subsequent small corrugation and shallow site registry. The amount of $6s$ component of the states slightly reduces upon co-adsorption, and simultaneously the d states become increasingly occupied, especially the d_{z^2}. In the phases with the cesium co-adsorbed with carbon monoxide the $5s$ slightly hybridises with the energetically close-lying 3σ forming a bonding and an anti-bonding hybrids; however the amount of hybridisation is small as expected at such deep binding energies.

The structure with the two carbon monoxide molecules in the unit cell, Ru (0001)-(2×2)-($1Cs_{ot}+2CO_{hcp,fcc}$), behaves very similarly to the case of one molecule, yet the binding energy of the second molecule is naturally lower than of the first one but still more bound than in the adsorbed phase of the carbon monoxide alone; this demonstrates one cesium can easily bind two CO molecules as seen in the experiments. The work function raises further from the value of the alkali-covered surface, and the bond lengths d_{C-O} and d_{C-Ru} increase towards the value of the separated phase as the effect from the cesium has to divided up to the two molecules.

We shortly studied also the the bonding of the inverted molecule, *i. e.* with the oxygen towards to the surface, both with and without the co-adsorbed cesium. However, the molecule desorbed without even a local minimum from both the on-top and hcp sites from the Ru (0001)-(2 × 2)-OC geometry and the co-adsorbed Ru (0001)-(2 × 2)-($Cs_{ot}+OC_{hcp}$) structure. Thus the possibility for a state with the rotated molecule as an intermediate in the oxidation reaction $^1/_2\,O_2+CO\rightarrow CO_2$

3.4.3 Co-adsorption of oxygen and carbon monoxide

The co-adsorption of oxygen and carbon monoxide has not only interest because of the oxidation reaction but also since the real catalysts always contain oxygen. The oxidation rate has been shown to be enhanced by the sub-surface oxygen, first using catalysts in high pressures – please see *e. g.* the references in Peden (1992) or Rodriguez and Goodman (1991) – and later using quantitative single-crystal measurements in the ultra-high vacuum (Böttcher *et al*, 1997). We performed calculations only in the Ru (0001)-(2 × 2)-($CO_{ot}+O_{hcp}$) co-adsorption structure shown in the Figure 3.101, and the Ru (0001)-(2 × 2)-($1CO_{ot}+2O_{hcp}$) – measured by Narloch, Held and Menzel (1994); the Ru (0001)-(2 × 2)-(2CO+1O) (Schiffer, Jakob & Menzel, 1997) has been realised in experiments but not calculated here. The relatively small repulsion between the adsorbed oxygen and carbon monoxide is

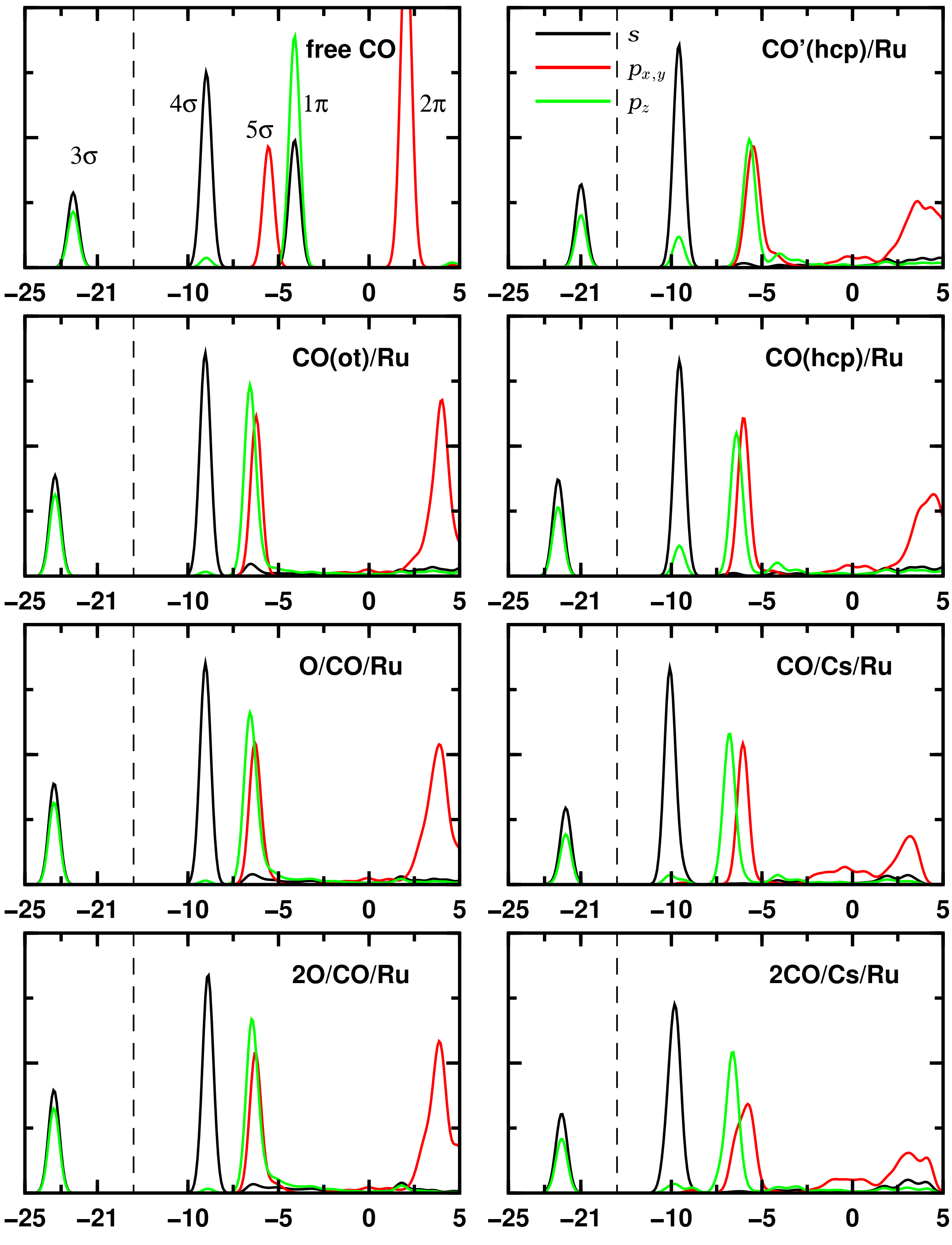

Figure 3.97: The density of states projected on the atomic orbitals of the carbon atom in different systems containing the carbon monoxide. "CO′(hcp)/Ru" refers to a CO molecule at hcp site with the geometry of the structure Ru-(2×2)-(Cs_{ot}+CO_{hcp}). The normalisation of the zero of energy is arbitrary in the case of the free molecule. The colours are s – black –, $p_{x,y}$ – red – and p_z – green

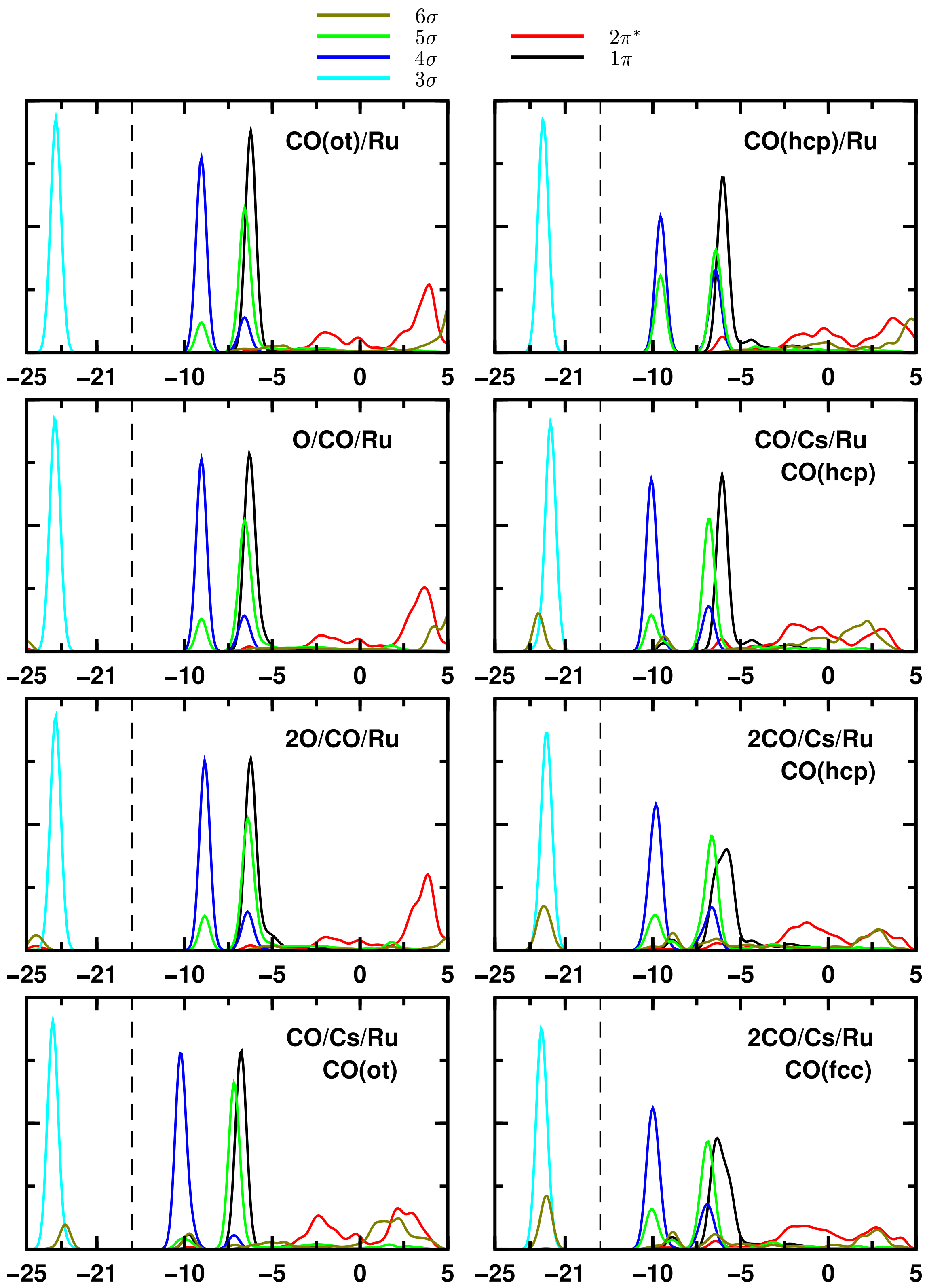

Figure 3.98: The density of states projected on the molecular orbitals of the carbon monoxide in different systems containing the molecule. The lines are lila – 3σ –, blue – 4σ –, green – 5σ –, brown – 6σ –, black – 1π – and red – 2π. The contributions of the π orbitals are symmetrised and halved

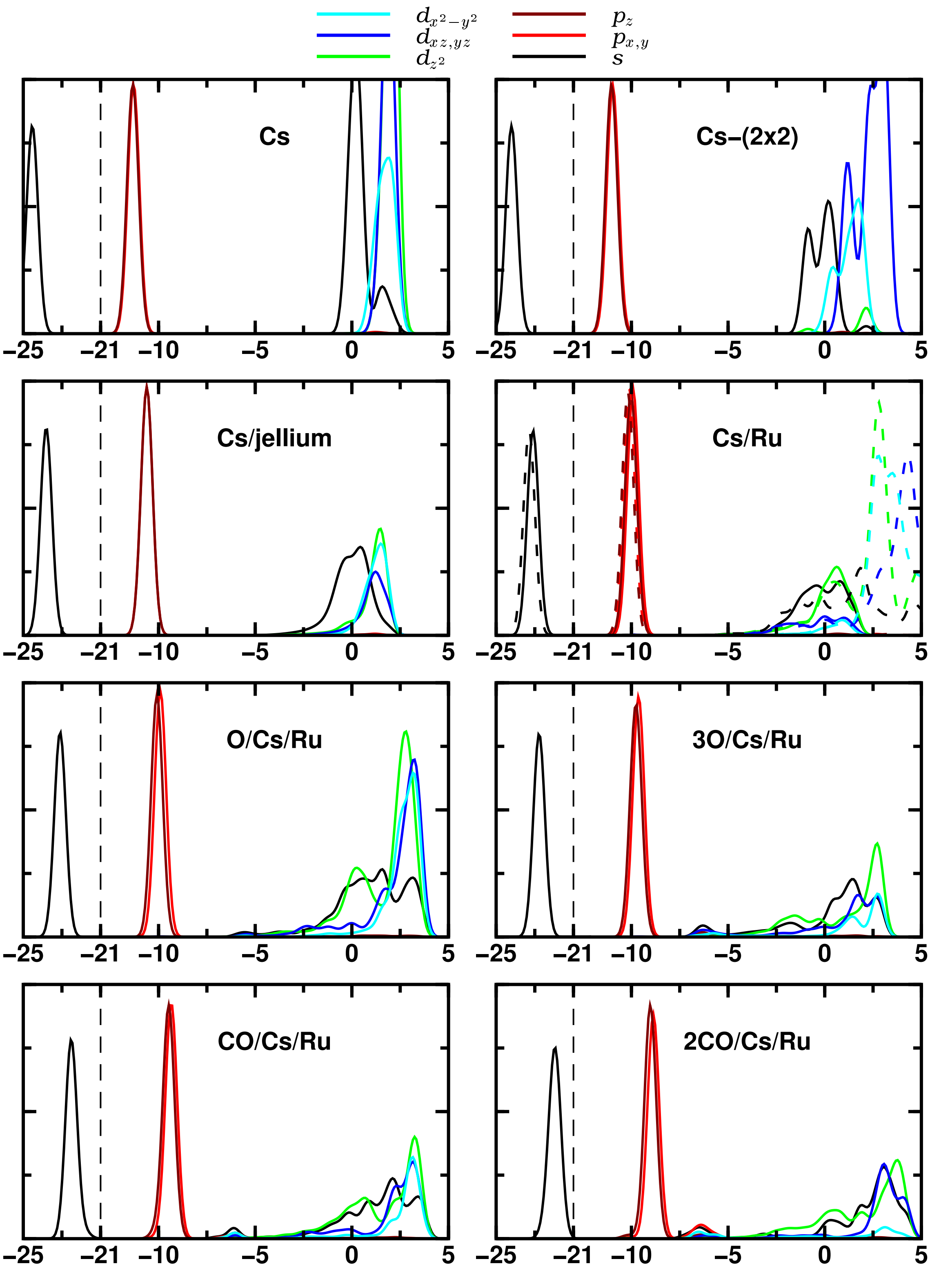

Figure 3.99: The density of states projected on the atomic orbitals of the cesium atom in different systems containing the cesium. The system "Cs" is a free atom in the (3×3) cell, "Cs-(2×2)" in the (2×2) cell. The system in "Cs/Ru" with the dashed lines is the cesium on ruthenium at the on-top site but in the geometry of the structure Ru-(2×2)-(Cs_{ot}+CO_{hcp}) but without the carbon monoxide; the system with solid line has been relaxed. The lines are black – s –, dark red – $p_{x,y}$ –, light red – p_z –, green – d_{z^2} –, blue – $d_{xz,yz}$ – and lila – $d_{x^2-y^2}$

Table 3.25: The integrals of the densities of states projected on the atomic orbitals. Ru_1 refers to the unique and Ru_2 to the three equivalent ruthenium atoms in the surface layer

Structure	Atom	s	$p_{x,y}$	p_z	d_{z^2}	$d_{xz,yz}$	$d_{x^2-y^2,xy}$
Ru (0001)-(2 × 2)-CO_{ot}	Ru_1	0.25	0.06	0.11	0.88	1.20	1.07
	Ru_2	0.24	0.06	0.04	1.06	1.20	1.07
	C	0.29	0.15	0.27			
	O	0.79	0.57	0.62			
Ru (0001)-(2 × 2)-CO_{hcp}	Ru_1	0.24	0.06	0.04	1.04	1.13	1.07
	Ru_2	0.24	0.07	0.05	1.09	1.10	1.07
	C	0.28	0.16	0.24			
	O	0.79	0.57	0.60			
Ru (0001)-(2 × 2)-(CO_{ot}+O_{hcp})	Ru_1	0.24	0.06	0.11	0.85	1.20	1.09
	Ru_2	0.24	0.07	0.05	1.10	1.08	1.07
	C	0.30	0.14	0.27			
	O	0.79	0.57	0.62			
	O	0.79	0.56	0.56			
Ru (0001)-(2 × 2)-(CO_{ot}+2$O_{hcp,fcc}$)	Ru_1	0.24	0.06	0.10	0.81	1.22	1.10
	Ru_2	0.23	0.07	0.07	1.10	1.05	1.08
	C	0.30	0.14	0.28			
	O	0.79	0.56	0.63			
	O	0.80	0.55	0.58			
	O	0.80	0.55	0.56			
Ru (0001)-(2 × 2)-Cs_{ot}	Ru_1	0.25	0.06	0.04	1.10	1.11	1.06
	Ru_2	0.24	0.06	0.04	1.09	1.10	1.06
	Cs	0.20	1.84	1.83	0.04	0.03	0.01
Ru (0001)-(2 × 2)-(Cs_{hcp}+CO_{ot})	Ru_1	0.25	0.07	0.11	0.93	1.14	1.10
	Ru_2	0.24	0.06	0.04	1.11	1.10	1.06
	Cs	0.16	1.85	1.84	0.04	0.02	0.01
	C	0.29	0.15	0.25			
	O	0.78	0.59	0.58			
Ru (0001)-(2 × 2)-(Cs_{ot}+CO_{hcp})	Ru_1	0.25	0.06	0.04	1.10	1.11	1.06
	Ru_2	0.24	0.07	0.05	1.12	1.08	1.07
	Cs	0.16	1.85	1.83	0.04	0.02	0.01
	C	0.27	0.17	0.22			
	O	0.78	0.60	0.56			
Ru (0001)-(2 × 2)-(Cs_{ot}+2$CO_{hcp,fcc}$)	Ru_1	0.25	0.07	0.04	1.11	1.11	1.06
	Ru_2	0.23	0.07	0.07	1.19	1.07	1.06
	Cs	0.15	1.86	1.84	0.03	0.01	0.01
	C_h	0.27	0.16	0.23			
	C_f	0.28	0.16	0.23			
	O_h	0.78	0.59	0.57			
	O_f	0.78	0.59	0.58			
Ru (0001)-(2 × 2)-(Cs_{ot}+O_{hcp})	Ru_1	0.25	0.07	0.04	1.11	1.10	1.08
	Ru_2	0.23	0.07	0.05	1.12	1.06	1.03
	Cs	0.18	1.85	1.83	0.05	0.03	0.01
	O	0.79	0.56	0.57			
Ru (0001)-(2 × 2)-(1Cs_{hcp}+3O_{hcp})	Ru_2	0.22	0.07	0.07	1.15	1.02	1.10
	Ru_1	0.22	0.08	0.09	1.22	0.94	1.12
	Cs	0.16	1.85	1.84	0.05	0.02	0.01
	O	0.79	0.56	0.56			

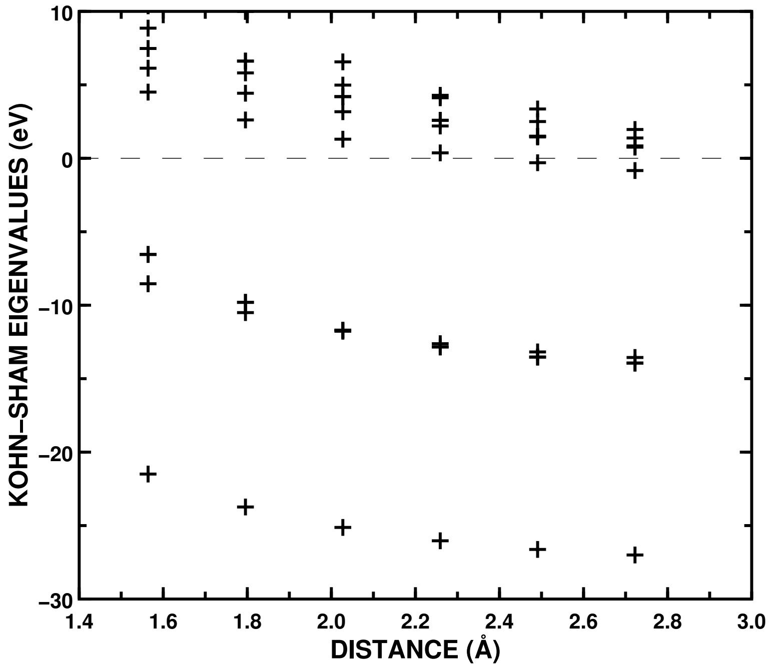

Figure 3.100: The Kohn-Sham eigen-values of a cesium atom in a hexagonal parallelepiped equivalent to the (2×2) cell used in the slab calculations. The free space between the atoms was reduced by applying a highly repulsive potential with the hexagonal shape. The zero of energy is set to the electro-static potential far away from the atom

Table 3.26: The occupation factors of different molecular levels of CO deduced from the projection of the Kohn-Sham states of the adsorption system on the molecular orbitals, and the mixing of 4σ and 5σ defined as the amount of molecular 5σ character of the 4σ in the adsorption system and vise versa

	Orbital						$4\sigma/5\sigma$	Charge
Structure	3σ	4σ	5σ	6σ	1π	$2\pi^*$	mixing (%)	at CO (e^-)
Ru (0001)-(2×2)-(Cs_{hcp}+CO_{ot})	0.998	0.988	0.883	0.062	0.969	0.350	5	−1.14
Ru (0001)-(2×2)-CO_{ot}	0.999	0.995	0.898	0.099	0.984	0.241	12	−0.88
Ru (0001)-(2×2)-(CO_{ot}+O_{hcp})	0.999	0.996	0.901	0.059	0.984	0.225	13	−0.75
Ru (0001)-(2×2)-(Cs_{ot}+CO_{hcp})	0.998	0.985	0.897	0.090	0.961	0.423	18	−1.48
Ru (0001)-(2×2)-CO_{hcp}	0.999	0.995	0.905	0.091	0.977	0.349	34	−1.28

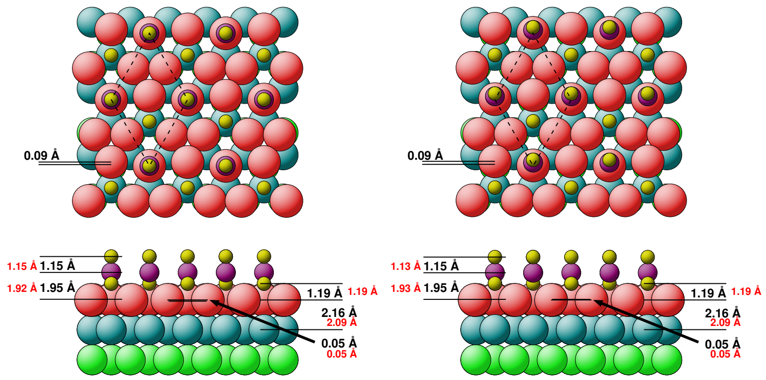

Figure 3.101: The geometry of the Ru (0001)-(2×2)-(CO_{ot}+O_{hcp}) from the density functional calculations; the experimental geometry is from Narloch, Held and Menzel (1995). The left panel gives the geometry without the static tilt *i. e.* with the full C_{3v} symmetry group and the right when the tilt is allowed

Table 3.27: The occupation factors of different levels deduced from the projection of the Kohn-Sham states of the adsorption system on the molecular orbitals, and the mixing of 4σ and 5σ defined as the amount of molecular 5σ character of the 4σ in the adsorption system and vise versa

	Orbital						$4\sigma/5\sigma$
Structure	3σ	4σ	5σ	6σ	1π	$2\pi^*$	mixing (%)
Ru (0001)-(2×2)-CO_{ot}	1.000	0.998	0.922	0.134	0.998	0.291	17
Ru (0001)-(2×2)-(CO_{ot}+O_{hcp})	1.000	0.999	0.923	0.150	0.998	0.279	14

possible since the change in the electro-static potential at the site of the carbon monoxide caused by the pre-adsorbed oxygen is weak. The interaction or mixing energy of the two is very small, 0.18 eV from our calculations, which can be understood since both oxygen and carbon monoxide are electro-negative adsorbates as can be deduced from the change in the work function of the separated (2×2) phases $\Delta\phi_{\mathrm{O/Ru}} = +0.36$ eV and $\Delta\phi_{\mathrm{CO/Ru}} = +0.61$ eV. The change in the co-adsorption phase 1CO+1O is +0.83 eV and in the 1CO+2O +1.37 eV, slightly smaller than the sum of the changes from the separated phases, which is probably since the ruthenium atoms cannot provide the charge and polarisation for both, and the electro-static repulsion might force the adsorbates to reduce their polarisation somewhat.

The occupation of the molecular levels in the co-adsorption phase, calculated as the projection of the co-adsorption states onto the orbitals of the free CO molecular, in the Table 3.27 support the very weak interaction between the co-adsorbates since the change from the case of only CO/Ru is very small, only a fraction of the total occupations. Furthermore the large energy separation of the 3σ level of the CO and the $2s$ state of the oxygen, together with a strong localisation of them, makes a hybridisation between the two very unlikely. This is confirmed in the Figure 3.102, which shows the orbital densities from the 3σ, O_{2p} and mixed $4\sigma/5\sigma$ states: indeed no mixing between the states from the co-adsorbates is seen. This is different for the co-adsorbed Cs and CO as we have seen above.

In their structural analysis of the Ru (0001)-(2×2)-(CO_{ot}+O_{hcp}) phase Narloch, Held and Menzel (1995) found a static tilt of the CO molecule from the surface normal; this tilt breaks the three-fold symmetry, and only a mirror-plane is preserved. We tried to reproduce their result, a tilt of 12.6°,

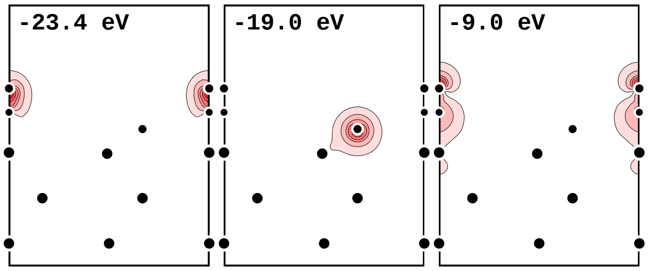

Figure 3.102: The orbital density of the deepest Kohn-Sham states in the structure Ru (0001)-(2 × 2)-(CO_{ot}+O_{hcp})

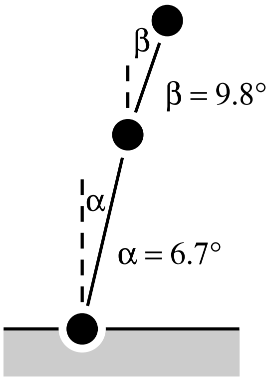

Figure 3.103: The final tilted geometry of the structure Ru (0001)-(2 × 2)-(CO_{ot}+O_{hcp}) when the lateral coordinates were allowed to relax

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