Coordination to Transition Metal Surfaces - A Theoretical Study

R. A. van Santen, Shell Development Company, Houston, Texas, USA

Summary

A theoretical framework is developed that describes the chemisorption of CO to transition metal surfaces analogous to the HOMO-LUMO concept of molecular orbital theory. An explanation is given for the experimental observation that CO adsorbs on top at the (111) face of Platinum, but bridge at the (111) face of Nickel. It is demonstrated that it is due to differences in the interaction with the d-valence electrons. Adsorption of Potassium changes the relative position of the adsorbate levels with respect to the Fermi level of the metal due to the positive charge of adsorbed Potassium. This changes the balance of the donating and back donating contributions to the adsorption energy of CO and tends to favor bridge coordination on Platinum as is found experimentally. The factors determining top or multiple adsorption of hydrogen are analyzed.

I. Introduction

Within the realm of surface science there is a rapidly growing body of new information generated by the study of well defined surfaces in systems of catalytic interest.[1]

In addition to comparative catalytic experiments, theoretical studies are needed that aim to develop conceptual understanding. This will contribute to establish fundamental principles in heterogeneous catalysis and may also provide a framework to be explored in the search for new catalysts.

The geometry of the adsorption complex plays a significant role in theories that attempt to explain changes in chemisorption caused by promoting ions, adsorbed moderators or alloying.[2]

Changes that occur can often be interpreted in simple geometric terms. The presence of additional electronic factors is sometimes invoked, but this area is still highly controversial.[3,4]

At present there is no simple theoretical method available that relates changes in binding geometry to alterations in the surface electronic structure not even on the level of the Hückel method that has found wide use in organic chemistry.

Here we explore such a relation using results of calculations on semi-infinite lattices that interact with Hydrogen and CO. We will study changes in chemisorption by promoting the surface with K.

The method used is an extension of Grimley and Pisani's[5,6] embedding method and Newns[7] Anderson model calculations on one dimensional arrays.

The adsorbate and metal surface are considered within the L.C.A.O. or tight binding approximation including only nearest neighbor interactions. We use a modified Anderson Hamiltorian, that includes explicitly changes in electrostatic interactions on the adsorbate and between adsorbate and neighboring surface metal atoms.

The semi-infinite f.c.c. metal lattice will be reduced to a Cayley lattice[8] using the Bethe lattice approximation.

Chemisorption to a transition metal surface involves interaction with essentially two valence electron bands. The broad s,p-valence electron band that contains approximately one electron per atom and the narrow d valence electron band system that has varying electron occupancy.

The quantum chemistry of coordination is first discussed as a function of valence electron-band filling by considering interaction with one valence electron band. Finally, chemisorption of CO to transition metals in the presence and absence of Potassium is analyzed.

The concepts of surface symmetry orbitals[9] or group orbitals appears to be very useful to understand changes in the relative bond strength of adsorbates with different coordination as the valence electron band occupation changes.

II. Method

We discuss shortly the method and most important expressions. If one includes electron-electron repulsion on the adsorbate and between the adsorbate and neighboring surface atoms one derives as expression for the adsorption energy:

$$E_{ads} = \Delta E - U_o n_o^\sigma \cdot n_o^{\sigma'} - \sum_{\sigma_i} \Sigma |P_{oi}^\sigma|^2 U_{oi} \qquad (2.1)$$

$$\Delta E = \sum_\sigma \left\{ \frac{1}{\pi} \int_{E_{min}}^{E_F} \eta^\sigma(E)dE + \sum_k (E_k^\sigma - E_F) - (\alpha_o - E_F) \cdot N_o^\sigma \right\} \qquad (2.2)$$

This expression can be used when one orbital is populated on the adsorbate. The general expression for $\eta^\sigma(E)$ is:

$$\text{arc tg } \eta^\sigma(E) = \frac{\text{Im} \frac{\det [0^\sigma - ES]}{\det [0_{latt} - ES_{latt}]}}{\text{Re} \frac{\det [0^\sigma - ES]}{\det [0_{latt} - ES_{latt}]}} \qquad (2.3)$$

and E_k^J are the discrete roots of $\det [0^J - ES]$ $\qquad (2.4)$

An expression closely related to (2.3) has been used by Callaway.[10] The matrix 0 has been discussed extensively[6]. The surface cluster is taken to be equal to the adsorbate and nearest neighbor surface orbitals. In the Bethe lattice approximation for a single valence electron band the indented lattice Greens functions are equal and become:

$$G = \frac{E-a}{2b} \pm \frac{1}{2b} \sqrt{(E-a)^2 - 4b^2} \qquad (2.5)$$

The − sign is used when E−a>o, + sign when E−a<o. The parameters a and b depend on the metal lattice. $b = Z\beta^2$, a and Z are given in Table I. α_m is the Coulomb energy integral of the metal atomic orbitals and β their overlap energy integral. The reduction process is illustrated in Figure 1. The general solution has been discussed in ref. 11. Z_s equals the number of metal atoms that are nearest neighbors of the metal atom interacting with the adsorbate excluding the metal atoms that interact with the adsorbate. Z equals the effective number of bulk neighbor atoms minus 1. The matrices O_{latt} and S_{latt} equal O^σ or S omitting the matrix elements involving the adsorbate orbitals. E_{min} is the bottom of the valence band, E_{max} the top and E_F the Fermi level. $\alpha_\circ$ is the adsorbate orbital energy before adsorption. $N_\circ^\sigma$ its occupation before adsorption, $n_\circ^\sigma$ after adsorption. $U_\circ$ is the one center repulsion integral at the adsobate, U_{oi} the two center repulsion integral between adsorbate and nearest neighbor metal atoms. P_{oi}^σ is the corresponding bond order. $\alpha_\circ^\sigma$ the adsorbate Coulomb potential and $\beta_{\circ i}^\sigma$ the overlap energy matrix elements are calculated as in the CNDO method[12]. In addition $\alpha_\circ^\sigma$ contains a term accounting for the image potential:

$$\alpha_\circ^\sigma = \alpha_\circ + U_\circ \cdot n_\circ^{\sigma'} + E_{im} \left| n_\circ^\sigma + n_\circ^{\sigma'} - Z_\circ \right| \qquad (2.6)$$

$$\beta_{oi}^{'\sigma} = \beta_{\circ i} - P_{\circ i}^\sigma U_{\circ i} \qquad (2.7)$$

$Z_\circ$ is the effective nuclear charge at the adsorbate.

Since $\alpha_\circ^\sigma$ and $\beta^{'\sigma}$ depend on the electron density, a self consistent method is used and the solutions are found in the restricted and, if necessary, in the unrestricted Hartree-Fock method.

The valence electron band structure of a group VIII metal is a relatively narrow partly filled d-band overlapped by a broad also partly filled s-band. The electron occupation of the d-band increases moving from left to right in the periodic system, the s-band occupancy is nearly constant at 1 electron per atom. As discussed earlier for Platinum and Nickel[4], with a d-band occupation of 9 electrons per atom, the d-band can be considered to consist of two sub-bands. A relatively narrow completely filled d_z2, $d_x2_{-y}2$ band and broader partially filled degenerate d_{xy}, d_{yz} and d_{xz} bands. The electron occupation of each band is 1 2/3.

We will simplify our discussion by considering only the interaction of the adsorbate with surface metal orbitals that are partially filled. Analogous to the familiar HOMO-LUMO concept in molecular orbital theory. So the interaction with the d-band will be considered to take place only with the d_{xy}, d_{yz}, and d_{xz} sub-band system.

At the (111) face each of the d_{xy}, d_{yz} and d_{xz} orbitals loose one of their 4 neighbors and for each orbital one lobe dangles from the surface towards the vacant positions (Fig. 2a). The degeneracy at the surface is lifted by interaction of these lobes, each from a different atom.[13] One finds one bonding and two anti-

bonding combinations as sketched in figure 2b.

III. Quantum Chemistry of Chemisorption

Dependence on Metal Coordination Number

Classical chemistry would predict that the bond strength decreases, if the coordination number of the surface metal atoms increases. Using small model clusters we have argued earlier[14] that this will depend amongst other on the electron occupation of the valence-electron orbitals and that the dependence can invert when the valence electron band becomes nearly filled. Tersoff and Falicov more recently found similar effects.[15]

For top adsorption we have investigated the dependence on Z_s for a Cayley tree with $a = o$ and $Z = 7$. The s-valence electron band contains one or two electrons per metal atom. The orbital on the adsorbate has also s-symmetry and contains one electron before interaction with the lattice. The results are presented in Figure 3. Whereas the bond strength increases with decreasing surface metal coordination for a half filled valence electron band, it is found to decrease if interaction takes place with a completely filled valence electron band. When the valence electron band is half filled, the change in bond order is found to oscillate as a function of distance from the adsorbate. The bond order of the metal-metal bond between the metal atom coordinated with the adsorbing atom and its nearest neighbors decreases. However it increases when the valence electron band is completely filled. We have interpreted this previously[14] as indicating that changes in localization energy determine the Z_s dependence for a half filled valence electron band, but depletion of anti bonding valence electron levels for the completely filled valence electron band.

For weak adsorption one derives:

$$\frac{1}{\ } \int^{E_F} dE \ arc \ tg \ \eta'(E) = - N \beta'^2 \rho_N(E_F) \qquad (3.1)$$

N is the adsorbate coordination number.

In our case N=1 and $\rho_1(E_F)$ is the local density of state (LDOS) on the surface atom at the Fermi level. $\rho_1(E)$ is plotted as a function of energy in Figure 4. For weak adsorption it is seen that the reversal in Z_s dependence as a function of band filling corresponds to a reversal in the relative magnitudes of $\rho_1(E)$ if the valence electron band becomes filled.

We have performed Hartree-Fock calculations for hydrogen interacting on top with the d_{xy}, d_{yz}, d_{xz} surface sub-bands at the (111)-face ($Z_s = 3$) of a f.c.c. crystal as a function of band filling. The results are compared with interaction at the (111)-face edges where two lobes of the orbitals are unsaturated ($Z_s = 2$).

Figure 6 shows inversion of Z_s dependence at a bulk band occupation number $n^b_{occ} = .97$.

strong. We also assume that interaction of two orbitals of different symmetry with one valence electron band can be considered independent. This is consistent within our approach since it is rigorously true within the Bethe lattice approximation.

Figure 7 illustrates the interaction of CO with the d_{xy}, d_{xz} and d_{yx} orbitals. We consider the top and bridge position. The parameters are chosen such that the d-band width and level positions of CO are reasonably reproduced. The parameters used in Figure 7 yield localized states outside d_{xy}, d_{xz} and d_{yz} bands for top as well as the bridging position.

The relative shifts of the 5σ orbitals do not correspond to their respective energy contributions. The latter are determined by the SSED's at E_F in agreement with expression (3.1) for weak adsorption. Respective energy contributions are bracketed in Figure 7e.
The inverse shift of the 5σ orbitals is compensated by a slightly lower occupation of antibonding levels in the top position than in the bridging position.

The maxima of the SSED's are seen to shift in a direction opposite to the shift in adsorbate levels, just as one expects to happen in Molecular Orbital Theory.

Figures 8 shows results for the interaction with the s-band. The width of the s-band has been chosen six times that of the d-band. The Fermi-levels of the s- and d-bands are, of course, equal and fix the relative positions of the bands with respect to each other.

The LDOS of the adsorbate 5σ orbital at the bridging position has its maximum at an energy slightly lower than on top position. The bond energy is, however, lower because of the slightly higher occupation of antibonding orbitals. Again the sequence in bond energies agrees with that expected from the SSED's before adsorption (Figure 5, $E_F=1$).

For completeness in Figure 8 the LDOS of the $2\pi^*$ orbital is shown. There is, of course, only a contribution to bonding in the bridge position, because only then a finite SSED exists with antisymmetric symmetry. In the first two columns of Table III, the individual contributions to the total energy are added. With our parameter choice the top position is favored over bridge.

This, indeed, is observed for the (111) face of Pt at low coverage.[10] Clearly the interaction with the d-valence-electron band is responsible for this effect.

V. Alkali Promotion

Addition of promotors (K) to the surface increases the number of neighbors of the surface atoms. This tends to decrease the bond strength between surface and adsorbate. If the difference in electronegativity is large compared to the overlap energy, this decrease, however, is small and the dominant effect is the change in potentials due to the charge on the promotor. We will study the effect of K coadsorption on the adsorption of CO within this approximation. Potassium has donated some of its charge to Pt. The resulting electric field around potassium

Dependence on Adsorbate Coordination Number

One expects a chemisorbed molecule to prefer sites such that the maximum coordination number agrees with its Van der Waals radius. This indeed is found from our calculations in the limit of strong chemisorption. Then the roots E_k (2.3) determine largely the bond energy. The bond strength then is $\sim N$.[16]

However, when chemisorption belongs to the intermediate case, valence electron band occupation changes are reflected in a behavior that follows more or less $N_{\rho_n}(E)$. $\rho_n(E)$ is the surface symmetry electron density (SSED) of the linear combination of atomic orbitals that interacts with the adsorbate orbital. They are plotted as a function of E in Figure 5 for the s valence electron band at the (111)-face of a f.c.c. crystal. For coordination to an orbital of s symmetry, the maximum of the SSED shifts to the left with increasing adsorbate coordination. As a consequence the lower coordination tends to become more favored with increased valence electron band occupation N_{el}[16] and/or weaker adsorbate interaction. In Figure 6 for Hydrogen interacting with the same d_{xy}, d_{yz} and d_{xz} surface sub-bands as in Figure 5a, these expectations are confirmed at the (111)-face comparing on top with three coordination. At higher surface unsaturation the increase in the SSED for on top coordination is so large, that it dominates.

Table II gives the contribution to the Hydrogen bond strength due to interaction with the s-band at the (111)-face of a f.c.c. with 1 electron per atom. The interaction is now rather strong, so three coordinated Hydrogen interacts more strongly than monocoordinated Hydrogen. Narrowing of the SSED by increased surface unsaturation increases the interaction on top, but decreases three coordination. The latter is opposite to the result found for interaction with d-electrons.

Our results can be summarized as follows:
- For strong chemisorption the localization energy and coordination number determine the bond strength.
- For weak or medium chemisorption the surface symmetry electron density at the Fermi level becomes more important.

IV. Chemisorption of CO to Transition Metals

The interaction with the CO molecule can be described as the sum of two contributions.[17] The first is due to overlap of the symmetric double occupied 5σ orbital located at the carbon atom, with metal surface orbitals. Since this interaction is accompanied by donation of electrons from 5σ orbitals into empty metal surface orbitals, this term is called the donating term. The second term is due to overlap of the surface electron density with the antisymmetric unoccupied $2\pi^*$ orbitals. This is the back donating term, since now electrons are transferred from the metal surface orbitals towards antibonding $2\pi^*$ orbitals. Our discussion is simplified by considering only the interaction of CO with surface metal orbitals that are partially filled. We will consider the interaction with the s- and d-bands separately. This is a valid approach as long as the chemisorptive interactions are not too

lowers the potential of the adsorbate levels and the Pt-atoms around potassium. Since the bulk Fermi level does not change, this will increase the charge on the neighboring surface atoms.

As can be observed in Table III and as expected from the changed relative energies, the interaction with the accepting $2\pi^*$ orbital increases, but with the donating 5σ orbital decreases. So we find that alkali adsorption induces a shift from top site to bridge site adsorption.

According to the experiment by Crowell, Garfunkel and Somorjai,[18] coadsorption of potassium not only shifts the adsorption geometry of adsorbed CO, it also increases the heat of adsorption. With our parameters, one is indeed able to reproduce such an effect. N. K. Ray and A. B. Anderson recently published related results, but ascribe this to a decrease of ionization potential of Pt.[20]

Bridge adsorption becomes favored if the workfunction of the metal as well as the interaction with the d-band decreases[4] as is the case for Nickel.[19] The total interaction of CO is less with Ni than Pt[1], because the decrease of the interaction with the d-band dominates.

It is of relevance to note that if the effect of Potassium were only an increased electron occuption at neighboring surface atoms, but no change in relative potential of the CO levels (Table III, case $\Delta V_{CO} = 0$), only changes in $\rho_N(E_F)$ determine the energy contribution. Now the energy contribution due to the interaction with the d-band decreases, but all interactions with the s-band increase. Then the total interaction of CO with Platinum is found to decrease upon Potassium coadsorption, contrary to experiment.

VI. Conclusion

We have developed an approach to the theory of chemisorption of CO to a transition metal surface analogous to the Hückel theory as applied to molecules.

Crucial for the understanding of CO chemisorption is the use of surface symmetry electron densities at the Fermi level, that assume the role of the lowest unoccupied molecular orbitals (LUMO) and highest occupied molecular orbitals (HOMO).

Chemisorption of CO to platinum can only be understood, if the interaction with the d-orbitals is taken into account. The dominant effect of K adsorption is a change in relative energies of adsorbate orbitals and the metal surface due to a direct electrostatic interaction.

In the case of hydrogen the relative interaction with the s-valence electron band is much stronger and the influence of the surface symmetry electron densities is much less.

We have used this earlier[4] to explain the increased interaction of Nickel with Hydrogen when compared with Platinum.

References

1. G. A. Somorjai, Chemistry in Two Dimensions: Surfaces, Cornell University Press, Ithaca, London, 1981.

2. P. A. Kilty, W. M. H. Sachtler, Catal. Rev. - Sci. Eng., $\underline{10}$, 1 (1974); W. M. H. Sachtler, R. A. van Santen, Adv. in Catal. $\underline{26}$, 69 (1977).

3. R. Burch, Acc. Chem. Research, $\underline{15}$, 24 (1982).

4. R. A. van Santen, Recl. Trav. Chim. Pays Bas, $\underline{101}$, 121 (1982).

5. T. B. Grimley, C. Pisani, J. of Phys., Solid State Phys. $\underline{7}$, 2831 (1974), C. Pisani, Phys. Rev. B, $\underline{17}$, 3143 (1978).

6. R. A. van Santen, L. H. Toneman, Int. J. of Quantum Chemistry, $\underline{12}$, Suppl. 2, 83 (1977).

7. D. M. Newns, Phys. Rev., $\underline{178}$, 1123 (1969); G. P. Muscat, D. M. Newns, Progr. in Surf. Sci. $\underline{9}$, 1 (1978).

8. R. Haydock, V. Heine, M. G. Kelly, J. of Phys. C.: Solid State Phys. $\underline{8}$, 2591 (1975); B. C. Khanra, Chem. Phys. Lett. $\underline{96}$, 76 (1983).

9. M. G. Kelly, Surface Science $\underline{43}$, 587 (1974); G. W. Gadzuk, NATO Advanced Study Institute Series, Plenum, N. Y., Physics Series B, vol. 16, 1976; L. Salem, R. Elliott, J. Mol. Structure $\underline{93}$, 75 (1983).

10. J. Callaway, Phys. Rev. $\underline{B3}$, 2556 (1971); M. Seel, G. Del Re, J. Ladik, J. Comp. Chem. $\underline{3}$, 451 (1982).

11. R. A. van Santen, J. of Phys. C.: Solid State Phys, $\underline{15}$, L513 (1982).

12. R. A. van Santen, J. Chem. Phys. $\underline{71}$ (1), 163 (1979).

13. O. Kahn, L. Salem, in "Proc. of the Sixth International Congress on Catalysis, London, 1976", vol. 1, 101 (1979).

14. R. A. van Santen, Surface Science, $\underline{53}$, 35 (1975).

15. J. Tersoff, L. M. Falicov, Phys. Rev. $\underline{B24}$, 754 (1981).

16. R. A. van Santen, W. M. H. Sachtler, Surface Science, $\underline{63}$, 358 (1977).

17. T. B. Grimley, in "Molecular Processes in Solid Surfaces", eds. E. Drauglis, R. D. Gretz, R. I. Jaffee, McGraw Hill, 1968, p. 299.

18. G. E. Crowell, E. L. Garfunkel, G. A. Somorjai, Surface Science $\underline{121}$, 303 (1982).

19. J. N. Allison, W. A. Goddard III, Surface Science $\underline{115}$, 583 (1982).

20. N. K. Ray, A. B. Anderson, Surface Science $\underline{125}$, 803 (1983).

Table I: Values of a and Z for Different Crystal Structures

	$\underline{a}$	$\underline{Z}$
s.c	α_m	9
f.c.c.	$\alpha_m + 4\beta$	16
b.c.c	α_m	16

Table II: Interaction Energies (eV) of H with surface of f.c.c. s band

COORDINATION	Z_s	UHF	n_o^σ	$n_o^{\sigma'}$	RHF	n_o
top	9	- .661	.95	.08	- .401	1.14
	8	- .743	.94	.10	- .562	1.12
triple	7	-1.604	.95	.15	-1.290	.90
	6	-1.589	.96	.14	-1.20	.88

$Z=16$, $\beta = -3$, $\beta' = -2$, $E_F = \alpha_m - \beta$, $U_o = 12$, $U_{o1} = 6$, $E_{im} = -1.5$
$\alpha_m = -8$, $\alpha_H = -12$.

Table III:

VAL BAND	MOL ORB	NO ALKALI COADSORBED		ALKALI COADSORBED							
				$\Delta V_{Pt} s = -.25$				$\Delta V_{Pt} s = -.5$			
				TOP		BRIDGE		TOP		BRIDGE	
		TOP	BRIDGE	$\Delta V_{CO} = -.25$	$\Delta V_{CO} = -.0$	$\Delta V_{CO} = -.25$	$\Delta V_{CO} = -.0$	$\Delta V_{CO} = -.5$	$\Delta V_{CO} = -.0$	$\Delta V_{CO} = -.5$	$\Delta V_{CO} = -.0$
s	5σ	- .439	- .293	- .413	- .424	- .267	- .276	- .385	- .409	- .246	- .260
	$2 \pi^*$	--	- .256	--	--	- .322	- .273	--	--	- .474	- .256
d	5σ	- .454	- .263	- .322	- .339	- .203	- .215	- .241	- .264	- .154	- .176
	$2 \pi^*$	- .444	- .492	- .490	- .410	- .565	- .472	- .531	- .375	- .628	- .444
ΔE		-1.337	-1.304	-1.225	-1.173	-1.357	-1.236	-1.157	-1.048	-1.440	-1.136

Bond energy contributions and total Bond energy ΔE (eV) of CO adsorbed to
(III) Face of Platinum. Effect of alkali coadsorption.
Parameters the same as in Figures 7 and 8, except:
$$\alpha_{5\sigma}(K) = \alpha_{5\sigma} + \Delta V_{CO}$$
$$\alpha_{2\pi^*}(K) = \alpha_{2\pi^*} + \Delta V_{CO}$$
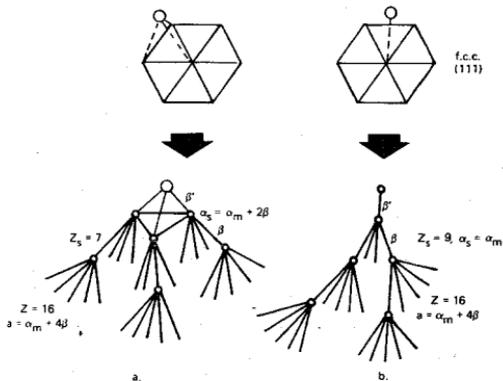$$\alpha_{Pt_{s,d}s}(K) = \alpha_{Pt_{s,d}} + \Delta V_{Pt^s}$$

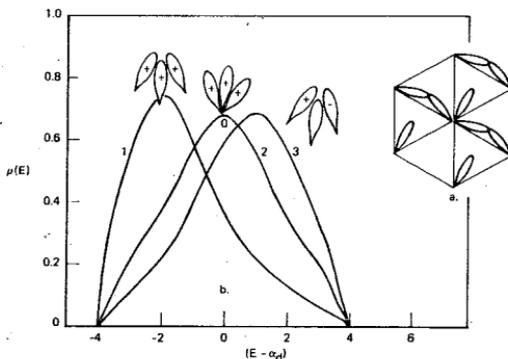Figure 1. Reduction of Top and Three Coordination of Hydrogen Atom at (111)-Face of f.c.c. s-Band to Cayleytree Models

Figure 2.

a. Dangling Orbital Lobes of d_{xy}, d_{yz} and d_{xz} Orbitals at (111) Face of f.c.c. Crystal.

b. SSED of Totally Symmetric (1), Non-Bonding (2) and Anti-Bonding (3) Combination of d_{xy}, d_{yz} and d_{xz} Orbitals. β'' is Overlap Energy Integral of Lobes Centered at Different Atoms.

$\beta = -1$, $Z = 4$
$\beta'' = -0.5$, $Z_s = 3$

a. Interaction Energy E_{ads} as a Function of Surface Metal Coordination (Z_s)

b. Change in Bond Order as a Function of Atom Number n from Adsorbate Bonded Metal Surface Atom. $Z_b = 8$, $N_{el} = 2$

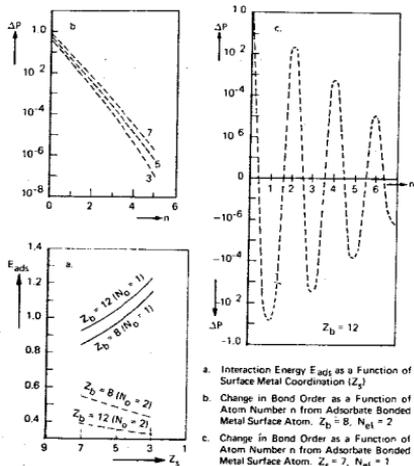c. Change in Bond Order as a Function of Atom Number n from Adsorbate Bonded Metal Surface Atom. $Z_s = 7$, $N_{el} = 1$

Figure 3. Interaction of Hydrogen with Cayleytree Defined in Text with Half $N_{el} = 1$ and Completely Filled Band ($N_{el} = 2$)
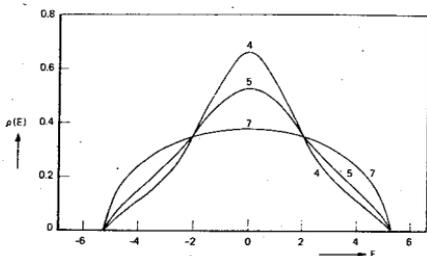$a_o = E_F$, $\beta = \beta' = -1$
No electron repulsion included

Figure 4. LDOS at Surface Atom of Cayleytree
The Numbers Denote Z_s. $Z_b = 8$
$a_m = 0$, $\beta = -1$

1 – Adsorbate Orbital of σ Symmetry, Three-Coordinated
2 – Adsorbate Orbital of π Symmetry, Two-Coordinated
3 – Adsorbate Orbital of σ Symmetry, Top
4 – Adsorbate Orbital of π Symmetry, Bridge

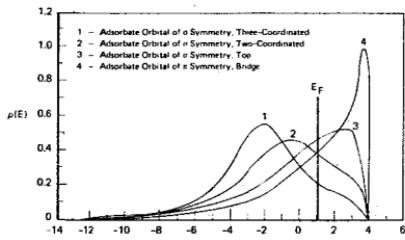Figure 5. Surface Symmetry Electron Densities (SSED) at the (111) Face of f.c.c. Crystal
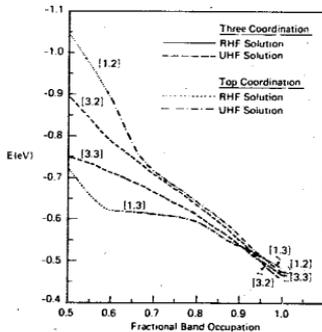

Figure 6. On Top and Three Coordination of Hydrogen Interaction with d_{xy}, d_{yz}, d_{xz} subband as a function of band occupation, (a, b)
a = coordination of a molecule
b = surface d orbital coordination
$Z = 4$, $\beta = -1$, $\beta' = -0.7$, $E_F - a_o = 7$
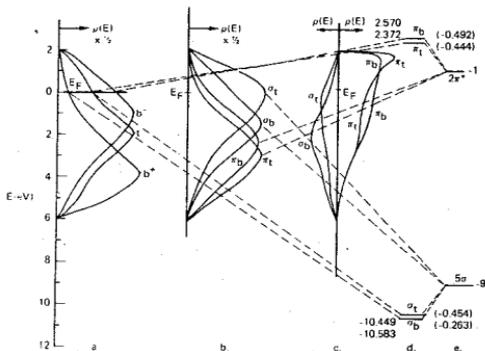$U_D = 12$, $U_{D1} = 6$, $E_{im} = -1.5$

Figure 7. Interaction of 5σ and 2π* Orbitals of CO with d_{xy}, d_{yz}, d_{xz} Subband of (111) Face of f.c.c. Metal (Pt)
Comparison between top and three coordination

a SSED's before interaction, b⁺ symmetric combination of three lobes centered at different atoms, t LDOS single lobe, b⁻ antisymmetric combination of three lobes centered at different atoms

b SSED's after interaction, t top position, b bridging position

c LDOS on CO after interaction

d Discrete eigen values after interaction

e Ionization potential and electron affinity before adsorption relative to E_F

$$Z = 4 \qquad \beta = -1$$
$$Z_s = 3 \qquad \alpha_d = -2$$
$$E_F = 0$$

5σ : $\beta_{d\sigma}^i = -7$, $\alpha_{5\sigma} = -19$; $U_0 = 10$. $U_{01} = 5$; $E_{im} = -1.5$
$2\pi^*$: $\beta_{d\pi}^i = .275$, $\alpha_{2\pi^*} = 1$. $U_0 = 8$. $U_{01} = 4$; $E_{im} = -1.5$

$$Z = 16 \qquad \beta = -3$$
$$a = -15 \qquad E_F = 0$$

5σ : $\beta_{s\sigma}^i = -1.9$. $\alpha_{5\sigma} = -19$. $U_0 = 10$. $U_{01} = 5$. $E_{im} = -1.5$
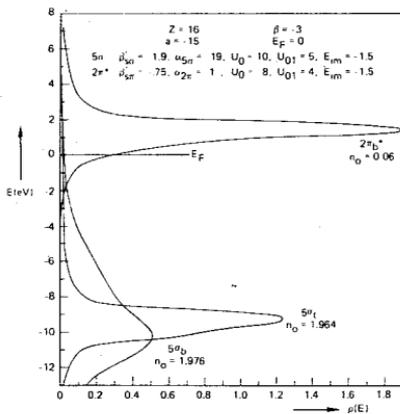$2\pi^*$: $\beta_{s\pi}^i = .75$. $\alpha_{2\pi} = 1$. $U_0 = 8$. $U_{01} = 4$. $E_{im} = -1.5$

Figure 8. Interaction of 5σ and 2π* Orbitals of CO with s-Band at (111) Face of f.c.c. Metal (Pt)
b: Bridging, t Top, n_0 Electron Occupation