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MODEL CALCULATIONS OF CHEMISORPTION ON TRANSITION METAL CLUSTERS

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Alloying of a transition metal with a non-transition metal affects the nature of the chemical bonds between the transition metal atoms in the surface and hydrogen or other atoms chemisorbed on them. The resultant changes in strength of the chemisorption bonds are due to (1) changes in delocalization of the metal electrons involved in the chemisorption bonds, (2) changes in the number of electrons available for such bonds. Our calculations have shown that the effects of alloying on chemisorption are different for monocoordinated adsorbates (ad-atom on top of metal atom) and tricoordinated adsorbates (ad-atom equidistant to three transition metal atoms) respectively. With localized bonds, alloying increases the strength of the former bond, but weakens the latter. As a result the ratio of monocoordinated to tricoordinated adsorbates, present in equilibrium at high coverage, is drastically increased by this type of alloying. The increase is much larger than expected on a geometrical basis only.

1. Introduction

Alloying a group-VII metal with a group-IB metal will change the binding energy of adsorbed atoms for both geometric and electronic reasons. If the adsorbate does not bind to a group-IB metal atom its average binding energy will decrease because of a decrease in average coordination to group-VIII metal atoms (ensemble effect). However, because of changes in electronic structure of the group-VIII metal atoms the binding energy of monocoordinated species is also expected to be affected (ligand effect).

Recently Sachtler [1], upon analysing the infra-red spectra of carbon monoxide adsorbed on PdAg alloys [2], has shown that the addition of Ag to Pd favours the monocoordinated (= linear) adsorbate of CO over the multicoordinated (bridged) complex to a much larger extent than would be predicted on a geometrical basis only. This example illustrates the more general observation that for adsorbates which are able to form several distinguishable complexes on a given transition metal, alloying always causes a drastic change in the relative concentrations of each of these complexes.

In the present paper we shall use model calculations based on the Anderson model of chemisorption [3–5] as well as Extended Huckel Molecular Orbital calculations [6] to investigate the effect of alloying on the heats of adsorption and,

hence, on the relative concentrations of two hydrogen complexes, viz. the mono-coordinated hydrogen, where the H atom sits on top of one transition metal atom, and the tricoordinated hydrogen where the H atom is located at a position equidistant to three transition metal atoms of the surface. Since the binding of hydrogen atoms to a metal surface is comparable to σ binding of hydrocarbons, a change in relative concentrations of the two types of ad-complex would have important consequences to catalysis. The effects induced by alloying are shown to be mainly due to changes in d band structure.
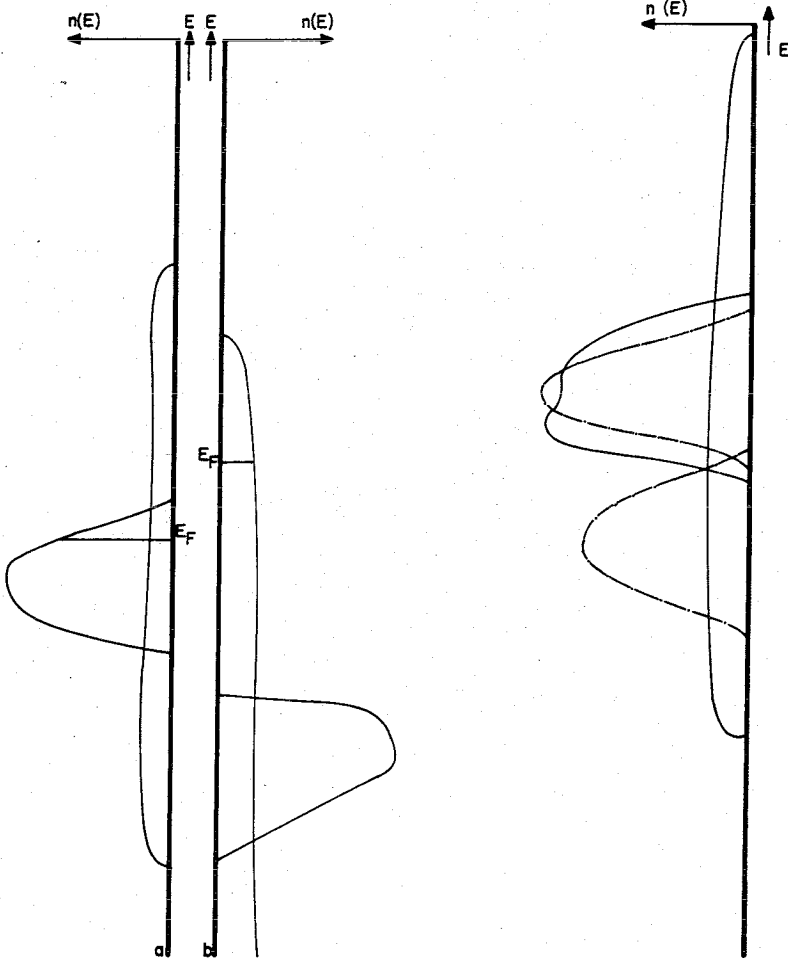

Fig. 1. Energy density of states $n(E)$ of valence electrons: (a) group-VIII metal; (b) group-IB metal.

Fig. 2. Band structure of an alloy: (————) monometallic; (– · – · –) alloy.

2. Electronic structure of alloys

As is illustrated in fig. 1, the electronic structure of the valence band of a group-VIII metal is a narrow partly filled d band overlapped by a broad, also partly filled, s–p band. Through the transition series the electron occupation of the s–p band is approximately constant. The d band of a group-IB metal is also narrow but completely filled. The average binding energy is usually larger than that in the group-VIII metals. In addition, a group-IB metal has a higher Fermi level than the group-VIII metal.

Upon alloying the Fermi levels have to become equal. This can cause some charge transfer between s–p band and d band and also a shift in average position of the d levels. If the d bands of the two metals are of different energy before alloying they will remain separated in the alloy, although sometimes some overlap might occur. This is accompanied by narrowing of the d band (see fig. 2), as is evident from UPS and XPS spectra [7]. Electron transfer from group-IB metal to group-VIII metal will give an exothermic contribution and band narrowing an endothermic contribution to the heat of formation of alloys.

3. Changes in binding energy of monocoordinated atoms

The electronic structure of the d band system of an alloy as introduced in the previous section can be well described by the coherent potential approximation [8]. Recent studies which are mainly concerned with the electron density of states at the surface of disordered alloys are based on this approximation [9,10]. We will use a very simple version of it to study the effects of narrowing and filling of the d band on the adsorption on monocoordinated species. We have calculated binding energies of hydrogen adsorbed on atom 1 of the bimetallic cluster shown in fig. 3. The binding energies are presented in fig. 4. They have been calculated for three
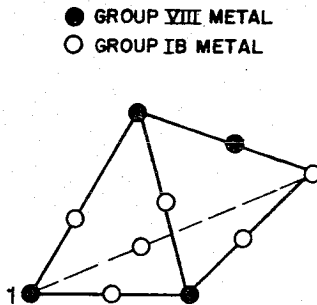

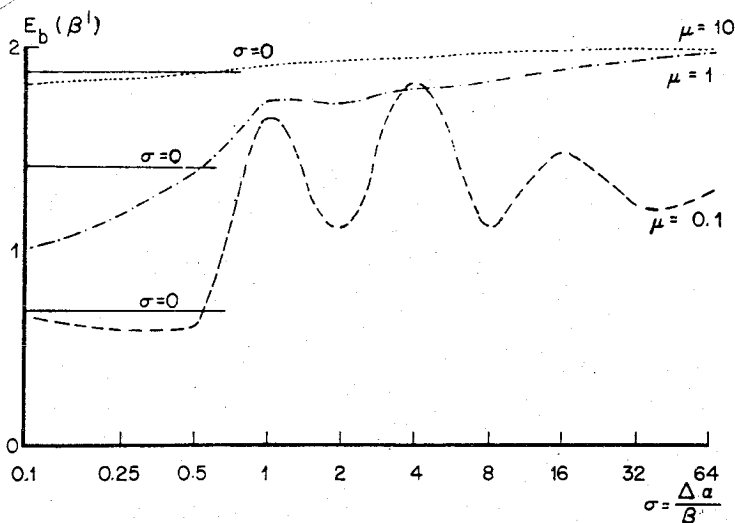Fig. 3. Bimetallic cluster: (•) transition metal; (o) group-IB metal.

Fig. 4. The effect of alloying on the binding energy of hydrogen to pyramid with one atomic orbital per atom: (———) values of E_b if $\sigma = 0$.

values of μ:

$$\mu = \beta'/\beta, \tag{1}$$

where β' is the overlap energy integral between the hydrogen atom and the metal atom and β is this integral between the metal atoms.

The parameter σ,

$$\sigma = \Delta\alpha/\beta \tag{2}$$

accounts for deviations from the rigid band model when metals are alloyed. $\Delta\alpha$ is the difference in Coulomb energy of the metal atoms and β is the overlap energy integral between the metal atoms, which is considered to be unchanged upon alloying. Each atom is considered to have one atomic orbital. The atom simulating a group-VIII atom contributes one electron, and the atom simulating a group-IB metal two electrons. The Coulomb energy of the hydrogen atom equals the energy of the highest occupied molecular orbital of the metal cluster.

If $\sigma > 0.6$ the binding energy is found to increase. For these values of σ two separate d bands can be distinguished [8b], each of which is narrower than the original band. The increase in binding energy observed can be simulated by a decrease in the number of metal atoms adjacent to the metal atom involved in chemisorption [5]. It has also been shown that for large values of μ complete filling of the metal orbitals results in a decrease in binding energy. Band filling and band narrowing then oppose each other.

The combined effect for two values of μ on the bond strength of the hydrogen atom bonded to position 1 of the pyramid in fig. 3 is shown in figs. 5a and 5b. N_{av}
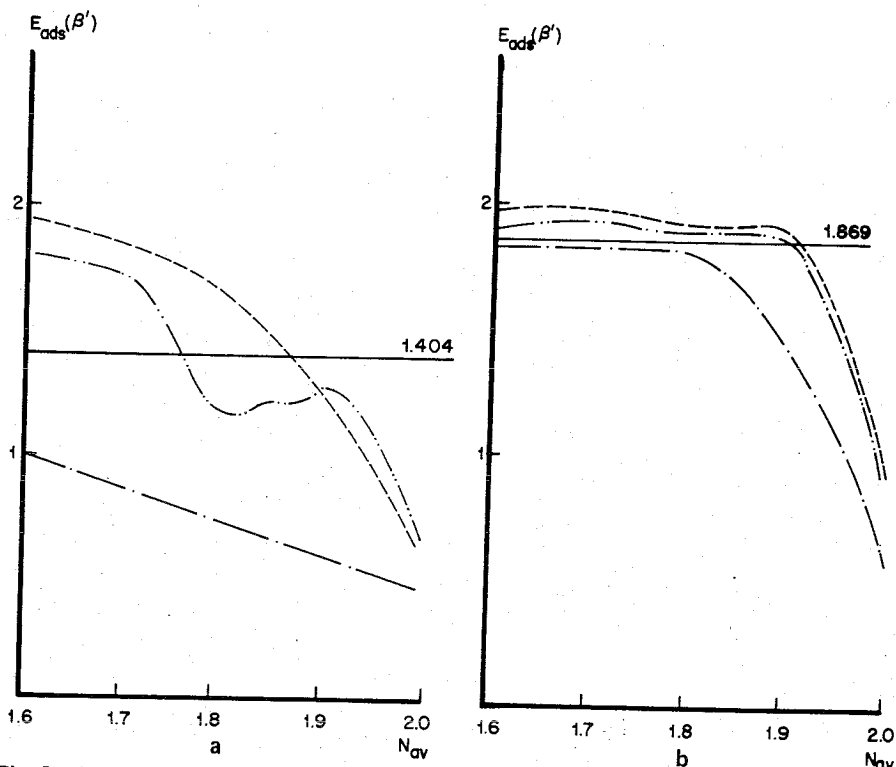
Fig. 5. The combined effect of band narrowing and electron transfer on the bond strength of hydrogen. Values of E_b: (———) on monometallic cluster; (— · — · —) on bimetallic cluster, $\sigma = 0$; (— · — · —) on bimetallic cluster, $\sigma = 4$; (— — —) on bimetallic cluster, $\sigma = 32$. (a) $\mu = 1$; (b) $\mu = 10$.

is the average number of electrons per cluster atom before adsorption. In fig. 5a the line of energy 1.404 β' represents the binding energy before alloying. In fig. 5b the corresponding value is 1.869 β'.

If the interaction between metal atom and hydrogen atom is much stronger than that between the metal atoms ($\mu = 10$), the binding energy is found to decrease only if the pyramid orbitals are nearly filled. The increase in binding energy due to band narrowing, hence the decrease in localization energy, is found to be larger than the decrease in binding energy because of orbital filling. Much the same results been observed previously [5] for adsorption on semi-infinite alloys. These effects are similar but less pronounced for smaller values of μ.

4. Changes in binding energy of tricoordinated atoms

The changes in binding energy of a tricoordinated species relative to a mono-coordinated species can be conveniently studied by reference to the adsorption

model presented in fig. 6. It consists of one central atom, the adsorbate, which interacts chemically with Z equal transition metal atoms, which in turn have Z' neighbours.

Again each metal atom contains one orbital of Coulomb energy α_m. The metal orbitals interact with each other by the overlap energy integral β. The orbital on the central atom representing the adsorbate interacts by overlap energy integral β' with the orbitals on the atoms adjoining the central atom. It has Coulomb energy α_H. Two electrons on the adsorbate orbital are supposed to interact with each other, as expressed by repulsion integral γ. We also consider the effect of inclusion of the overlap integrals S between the metal orbitals on the calculated results.

The Anderson model sketched above is solved for fixed values of α_H, α_m, γ and β':

$$\gamma/\beta' = -3.44, \quad (\alpha_H - \alpha_m)/\beta' = 2.12.$$

These values are representative of the interaction of a hydrogen atom with the d electrons of a transition metal. The solution of this model has been outlined previously [5] and is very similar to that adopted by Einstein [11]. A short discussion will be given in Appendix A. Fig. 7 shows exact solutions of the binding energy expressed in units β' for two situations as a function of μ defined in eq. (1).

If the metal-atomic orbitals are half filled the binding energy increases with increasing μ. The difference in binding energy between tri- and monocoordinated species becomes smaller as the adsorption strength increases. The behaviour is com-
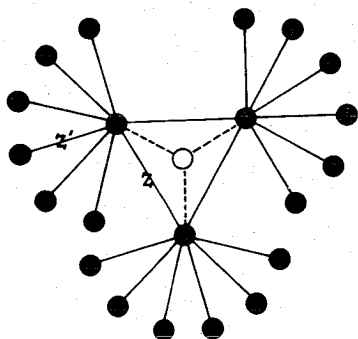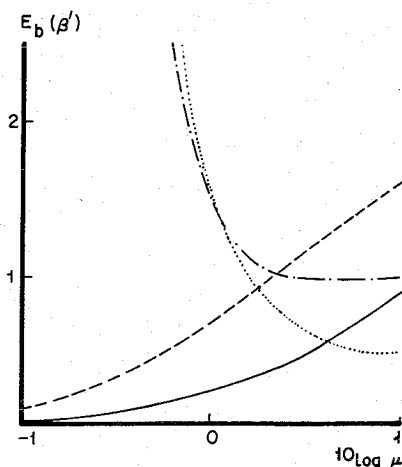

Fig. 6. Model cluster.

Fig. 7. Binding energy for cluster of fig. 6 as a function of μ (energy unit β'; $S = 0$). Metal atomic orbitals contributing 1 electron: (———) $Z = 1$, $Z' = 6$; (- - - - -) $Z = 3$, $Z' = 6$. Metal atomic orbitals contributing 2 electrons: ($\cdots\cdots$) $Z = 1$, $Z' = 6$; (— · — · —) $Z = 3$, $Z' = 6$.

Table 1
Relative changes in binding energy

	μ						
	4	5	6	7	8	9	10
$Q'(1.4)$	1.15	1.19	1.21	1.23	1.23	1.23	1.23
$Q\ (1.4)$	1.132	1.12	1.11	1.10	1.09	1.08	1.07
$Q\ (3.6)$	1.8	1.65	1.54	1.44	1.40	1.35	1.32
$Q'(3.6)$	3.77	3.8	3.74	3.64	3.51	3.38	3.26
$Q'(3.4)$	3.76	3.77	3.69	3.58	3.45	3.28	3.20

$$Q(a, b) = \frac{E_{ads}(Z = a, Z' = b, S = 0)}{E_{ads}(Z = 1, Z' = 6, S = 0)}, \quad Q'(a, b) = \frac{E_{ads}(Z = a, Z' = b, S = 0.25)}{E_{ads}(Z = 1, Z' = 6, S = 0.25)}.$$

pletely different if the metal-atomic orbitals contribute two electrons. The binding energy now increases as μ decreases. This feature has been explained elsewhere [5]. It is due to an increase in rebonding energy and the absence of a localization energy for two electrons.

If alloying results only in electron transfer to orbitals involved in bonding an adsorbate, the model predicts an increase in binding energy provided μ is small. This suggests a possible explanation of some apparently contradictory experimental results on Pt/Sn alloys. It has been observed experimentally [12] that the binding energy of oxygen atoms bonded to Pt atoms upon alloying with Sn increases. This state of chemisorption of oxygen onto Pt is apparently of the weak adsorption type. Donation of electrons of Sn to Pt dominates the adsorption. The binding energy of CO, however, is found to decrease upon alloying [13]. CO is bonded strongly and mainly by monocoordination to Pt [14].

If the valence band remains partly filled, alloying with a partner which has a weaker metal–metal interaction would give an increase in binding energy of both tri- and monocoordinated species. Charge transfer favours monocoordinated species.

Table 1 shows that changes in the relative energies of the two complexes can be due not only to transfer but also to localization of the electrons. Binding energies of hydrogen are compared upon changing Z' from 6 to 4. The monocoordinated species is found to increase in energy, whereas the tricoordinated species shows a decrease in binding energy. Inclusion of overlap S has a strong influence on the results of the calculations, but does not change the direction of the effects under discussion. Apparently the rebonding energy of adsorption complex dominates over the localization energy of the triangle of metal atoms in adsorption.

5. Extended Hückel molecular orbital calculations

Since the energy with which an adsorbate is bound to a transition metal is determined by d as well as s—p electrons, the combined effect of charge transfer and d-electron localization has been studied with the Extended Huckel method. The results are summarized in Talbe 2. The bimetallic clusters considered are similar to that shown in fig. 3. Each group-IB metal atom contributes 11 electrons to the metal clusters. The only other difference between a group-IB metal atom and a group-VIII metal atom considered is a much larger Coulomb potential of a d electron in the former (α_d(VIII) = 10.5 eV, α_d(IB) = 15.0 eV). Details of the calculations are presented in Appendix B.

Table 2 gives the difference in energy of binding to a bimetallic and a monometallic cluster as a function of the number of electrons per transition metal atom. No results are presented for electron occupation larger than 8, since outside that area we consider the Extended Huckel calculations unreliable (see Appendix B). Monocoordinated species are found to increase in energy, tricoordinated species to decrease in energy. The figures in the column headed "tri (lig.)" denote the change in energy if atoms directly coordinated with the hydrogen atom are transition metal atoms but their neighbours are replaced by IB metal atoms. The column headed "tri (ens.)" shows what happens if one of the transition metals involved in bonding is replaced by a IB metal atom. In agreement with expectations the decrease in binding energy is larger in the latter case than in the former. The calculations including s and p electrons again show that monocoordinated species can become favoured over multicoordinated species even if there is no replacement of atoms involved in the chemisorption complex. This orientation effect is only due to changes in electronic structure. Since the d band remains partly filled, the dominating effect is d-electron localization on the group-VIII metal atoms [5].

Table 2

Differences in binding energy of a hydrogen atom bonded to a bimetallic cluster and to a monometallic cluster, ΔE (bi) — ΔE (mono) (energy unit eV) (α_H = −10 eV)

Number of electrons [a]	Mono	Tri (lig.)	Tri (ens.)
2	+0.45	−0.15	−0.45
3	+0.46	−0.20	−0.77
4	+0.25	−0.24	−0.66
5	+0.20	−0.02	−0.33
6	+0.12	−0.12	−0.36
7	+0.12	−0.31	−0.55
8	+0.02	−0.11	−0.49

[a] Number of valence electrons per transition metal atom.

6. Conclusion

Both filling of the d band and d-electron localization are shown to be able to orient adsorbates which can in principle have different coordination on a metal surface. As long as d-band filling is not complete, d-electron localization can have very pronounced effects. The latter concept may be of great significance to catalysis, since it possibly explains why alloying of two active metals with each other does not impart the catalytic behaviour expected from averaging the properties of the pure metal [17].

The finding that orientation of an adsorbate can result from a change in electronic structure shows that the selectivity of a catalytic reaction can also depend on a ligand effect.

Appendix A

The calculation of the binding energy in the cluster of fig. 6

Ignoring the interaction with adsorbing atoms, the eigenvalues of clusters belonging to the eigenfunctions which are totally symmetric with respect to the central atom are found to be:

$$x^{\pm} = \lambda\{(1/(1 + 2S) - Z'S(1 + 2S) \pm [(1/(1 + 2S)^2) + Z'(1 + 2S - 2S^2)$$
$$+ 2Z'^2S^2(1 + 2S)^2]^{1/2} \times [1 + Z'S^2(1 + 2S)]^{-1}\},$$

with $\lambda = \beta - \alpha S$. These eigenfunctions $\phi\pm$ have the following matrix elements with the central atom orbital ϕ_H:

$$\langle\phi^{\pm}|H|\phi_H\rangle = \beta'(2ZZ')\left[(x^{\pm}S - \lambda)\bigg/\left(\frac{2\lambda}{1 + 2S} - x^{\pm}\right) + S\right]$$

$$\times \left[1 + (\lambda - x^{\pm}S)^2 Z'(1 - 2S)\bigg/\left(\frac{2\lambda}{1 + 2S} - x^{\pm}\right)^2\right]^{-1/2}.$$

The adsorbate atom interacts only with these two orbitals and the problem is therefore reduced to that of a linear chain of three unequal atoms with Coulomb integrals x^+, α_H and x^- and overlap energy integrals $\langle\phi^{\pm}|H|\phi_H\rangle$. For the cases where the metal cluster orbitals are half filled or doubly occupied this problem can be exactly solved.

Appendix B

Details of the Extended Huckel Molecular Orbital calculations

In EHMO theory molecular orbitals and energies are found by solving the eigen-value problem:

$$(H-ES)\,(c) = 0.$$

H is a matrix, with valence state ionization potentials of the atomic orbitals, α_i, as diagonal matrix elements. For the non-diagonal matrix elements we have used the customary approximation [15]:

$$H_{ij} = 0.875\,(\alpha_i + \alpha_j)S_{ij}.$$

The overlap matrix elements S_{ij} have been computed from atomic wave functions consisting of one Slater function. The exponential coefficients, ζ_i, of the s and p functions have been set at 1.5 and 1.83 respectively, as given by Clementi et al. [16]. For the d orbital we have chosen 3. This value is slightly lower than the tabulated one for the 5d orbital of Pt. With these parameters we calculated a d bandwidth of 2.38 eV of the clusters considered, which is a reasonable value if one takes into account the low average number of neighbours of the metals. Clementi's value gives an unrealistically small d bandwidth. There is no unequivocal means of selecting the parameters α_i. We have chosen $\alpha_p - \alpha_s$ such that for a mono-metallic cluster the lowest number of holes in the d band is obtained (8 holes)

Table 3
Binding energy of hydrogen (eV) to monometallic cluster with: $\alpha_d = -10.5$; $\alpha_s = -8.5$; $\alpha_p = -4.5$ and $\zeta_d = 3$; $\zeta_s = 1.5$; $\zeta_p = 1.83$

Number of electrons per metal atom	$\alpha_H = -7.6$		$\alpha_H = -10$		$E_{coh.}$ pyramid
	Mono	Triple	Mono	Triple	
1	3.814	4.191	2.22	3.46	15.40
2	3.62	4.33	2.52	3.77	23.06
3	3.66	4.36	2.57	3.79	29.28
4	3.21	3.92	2.79	3.45	33.92
5	3.26	3.92	2.95	2.88	34.78
6	3.27	3.93	2.99	3.56	34.06
7	3.24	3.74	3.04	3.48	32.51
8	3.39	3.68	3.20	3.332	28.53
9	3.09	3.18	2.80	2.86	21.19
10	3.03	3.09	2.95	2.77	10.64
11	1.98	1.215	3.184	1.92	12.90

with 10-electron occupation per atom. In addition we have chosen α_d such that the average position of the d electrons resembles that of Pt. The calculations have been made for a fixed metal atom distance of 2.76 Å and a metal–hydrogen distance of 1.76 Å. The former is the nearest neighbour distance between Pt atoms in bulk metal, the latter is the average sum of the atomic radii. As can be seen from table 3, these values of parameters α_i yield a dependence of cohesive energy on electron occupation per atom in rough agreement with that found experimentally, except if the number of electrons is increased from 10 to 11, which corresponds to changing from a group-VIII metal to a IB metal. Such an increase is due to transfer of electrons from the s shell to the d shell. These effects are to be ascribed to the neglect of electron occupation dependence of the parameters and have to be considered an intrinsic defect of the method used.

Table 3 further shows that in general triple-coordinated hydrogen is more strongly bonded than monocoordinated hydrogen except at high electron occupation. However, the binding energy of monocoordinated hydrogen can increase upon increasing the electron occupation per atom from ten to eleven, which does not agree with experimental observations [18]. This disagreement has the same cause as the artefacts found in the cohesive energy at high electron occupations per atom.

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