PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The Quantum-Chemical Basis of the Catalytic Reactivity of Transition Metals [and Discussion]

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Phil. Trans. R. Soc. Lond. A 1992 **341**, 269-282
doi: 10.1098/rsta.1992.0100

The quantum-chemical basis of the catalytic reactivity of transition metals

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State of the art computational quantum-chemical methods enable the modelling of catalytically active sites with an accuracy of relevance to chemical predictability. This opens the possibility to predict reaction paths of elementary reaction steps on catalytically active surfaces. The results of such an approach are illustrated for a few dissociation and association reactions as they occur on transition metal surfaces. Examples to be given concern CO dissociation, carbon-carbon coupling and NH_3 oxidation. Reaction paths appear to be controlled by the principle of minimum surface atom sharing.

1. Introduction

Microscopically, a generic catalytic reaction consists of a self-regenerating reaction cycle built of elementary reaction steps. The catalytic reaction cycle starts with molecular adsorption and is followed by dissociation and recombination of adsorbed molecular fragments. The cycle is closed by desorption of the product molecules (Boudart & Djéga-Mariadassou 1984). The selectivity of a catalyst depends, among other factors, on the rules of dissociation and recombination.

We review the electronic factors that control chemisorption of molecules and atoms on transition-metal surfaces to use as a basis for an analysis of the rules that determine the reaction paths of dissociation and association.

A wide body of excellent reviews exist summarizing the experimental data on chemisorption phenomena (Ponec 1975; Somorjai 1981; Ertl 1983, 1990). Also many theoretical reviews are available (Hoffmann 1988; Shustorovich 1990; Norskov 1992; van Santen 1991). The transition-metal valence electrons of relevance to surface chemical bonding are contained in a relatively narrow d-valence band and a broad partly overlapping s, p-valence electron band. The number of d-valence electrons may vary to a maximum of ten valence electrons per atom. A tight-binding description, in which the metal one-electron wave functions are considered to be a linear combination of atomic orbitals, appears to mimic the electronic properties of the surface d-levels relevant to chemisorption reasonably well (Newns 1969; Grimley & Torrini 1973). For example, as expected, an orbital of an adsorbing molecule interacts to produce bonding as well as antibonding fragment orbitals (Hoffmann 1988; van Santen & Baerends 1991; van Santen & de Koster 1991). For transition-metal surfaces one observes experimentally that the interaction-energy with adsorbates decreases as the d-valence electron-band becomes more occupied. This is due to the gradual filling of antibonding surface fragment orbitals.

Phil Trans. R. Soc. Lond. A (1992) **341**, 269–282

Printed in Great Britain

A tight-binding description serves less well for the *s-p*-valence electrons. To a first approximation the electrons in these broad bands behave as free electrons. The electron concentration per atom is more or less constant across the transition-metal series and equal to approximately one electron per atom.

In the jellium model, which describes the metal as a free-electron gas (Lang & Williams 1978; Lundquist *et al.* 1979; Norskov & Lang 1980; Norskov 1982; March 1986) electron-transfer between metal surface and adsorbate is assisted by the screening of the resulting adsorbate charge by the surface image charge generated in the free-electron gas. Charge-transfer is especially important for atomic adsorbates, with their low unoccupied atomic orbitals. However, we will see that it is also very important for the dissociation of molecules.

Both molecular as well as atomic chemisorption energies change with metal as well as surface topology. However, the changes in interaction energy of chemisorbed molecules are usually significantly less than that of chemisorbed atoms. Also, the bond energy of admolecules to the surface is usually less than that of adatoms. This difference is essential for the dissociation of a diatomic molecule, because the energy required to break the molecular bond has to be recovered by the interaction of the resulting metal atoms with the metal surface. Only when the sum of the adatom energies exceeds that of the adsorbed molecule dissociation will become thermodynamically feasible (Benziger 1980; van Santen *et al.* 1990).

We discuss results obtained with semi-empirical methods (Hoffmann 1988; van Santen & de Koster 1991) as well as first principle quantum-chemical methods (Baerends & Ros 1973, 1975; Blomberg & Siegbahn 1983; Brandemark *et al.* 1984; Hermann *et al.* 1985; Panas & Siegbahn 1988; Panas *et al.* 1989; Yang & Whitten 1989, 1991). Results obtained by both methods lead to the same picture of surface reactivity. The main restriction of first principle approaches is the limited size of the metal clusters that can be studied at present. Because of size limitations semi-empirical calculations, which can treat larger clusters but are limited due to their dependence on parametrization, will continue to have to be used. For this reason results as obtained with the ASED-method (Andersen 1974, 1975), which is an extension of the extended Hückel method (Hoffmann 1963) are also presented. In §2 a short discussion will be given on the crucial point of cluster choices.

2. Molecular versus atomic adsorption

(*a*) *The dependence on d-valence electron occupation*

The generally high average energy of the LUMO (lowest unoccupied molecular orbital) of a molecular adsorbate as CO will usually result in the occupation of only bonding surface-fragment orbitals. As the d-valence electron occupation increases, this interaction will increase. The interaction with the LUMO is often called electron-backdonation, because admixture of LUMO with surface orbitals results in a partial occupation of the LUMO which is naturally empty before adsorption.

The higher energy of the LUMO of a molecule in comparison to that of its constituent atoms, implies that the energy for electron transfer to the molecule is less favourable than in the case of atoms. For example, for CO coordinated C-end down to a Co cluster (van Santen & Zonnevylle 1992; Zonnevylle & van Santen 1992) using the first principle Amsterdam local density approximation (LDA) code (Baerends *et al.* 1973; Baerends & Ros 1973, 1975), figure 2*a* shows the increasing fractional orbital occupation of the $2\pi^*$ LUMO of CO and the total overlap population between $2\pi^*$ and

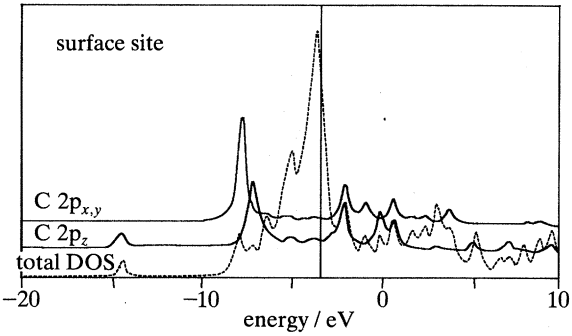

Figure 1. Local density of state C $2p_x$, $2p_y$ and $2p_z$ atomic orbitals of C adsorbed to a nine atom Co cluster (z direction is surface normal). C is three fold coordinated 0.1 nm from surface plane. Results are due to a local density approximation calculation (Zonnevylle *et al.* 1990). Note the electron densities around 5 eV below the Fermi level that correspond to the maxima of the bonding adatom-surface electron-density distribution. The maxima corresponding to the antibonding electron-density distributions are approximately 2 eV above the Fermi level.

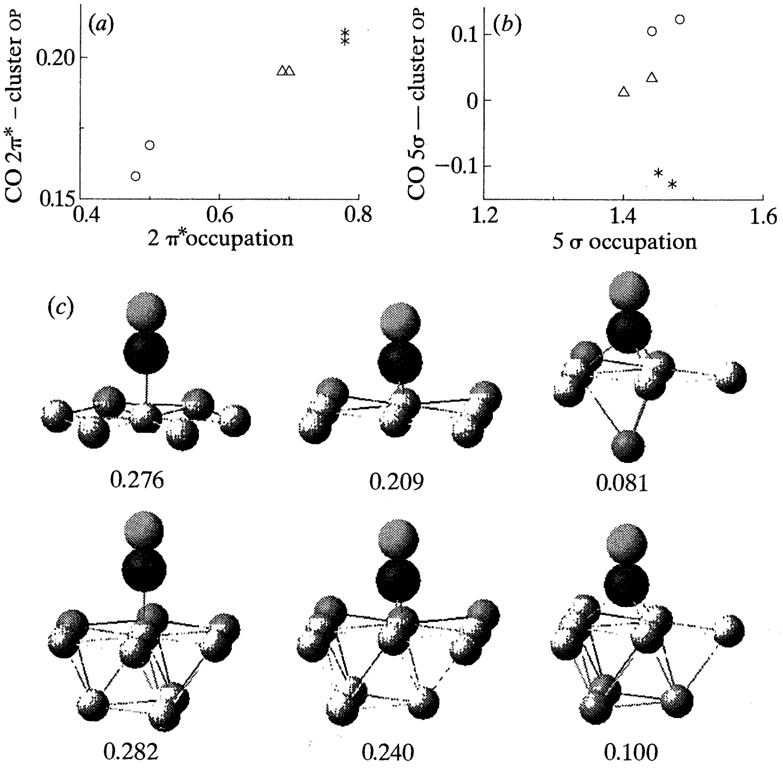

Figure 2. (*a*) $2\pi^*$-orbital population (OP) and $2\pi^*$-surface orbital overlap population of CO adsorbed to a Co cluster as a function coordination. The cluster simulates a (111) surface (van Santen & Zonnevylle 1992), see also (*c*). (*b*) 5σ-orbital population and 5σ-surface orbital overlap population of CO adsorbed to a Co cluster as function of coordination. The cluster simulates a (111) surface (van Santen & Zonnevylle 1992), see also (*c*). In (*a*) and (*b*): ○, top; △, bridge; *, hollow. (*c*) Clusters and geometries used in (*a*), (*b*) and figure 3. Within brackets total C–Co orbital overlap population (van Santen & Zonnevylle 1992).

all of the cluster orbitals. The fractional $2\pi^*$ orbital occupation reaches a value of close to 0.5 in the hollow high-coordination site. The relatively small values of the fractional occupation-number are indicative for the bonding nature of the $2\pi^*$-surface interaction, i.e. filling primarily adsorbate-surface bonding levels. This also follows from its increases with higher coordination number to the surface and the corresponding increase in $2\pi^*$-surface cluster orbital overlap population.

As illustrated in figure 1 in contrast to the molecular case, because of the low value of the average energy of the screened atomic LUMOs (a carbon atom in this case) with respect to the cobalt metal Fermi level now adatom–metal bonding as well as antibonding levels are occupied. Again in contrast to the molecular case an increase in d-valence electron occupation will increase the occupation of antibonding d-orbitals thus decreasing the interaction energy. However, the lower energy of the screened atomic orbitals compared with the molecular LUMOs contributes to the fact that adsorbate–surface interaction energies are greater than for molecules.

For a molecule, the interaction of its highest occupied molecular orbitals (HOMO), which are nearly always bonding combinations of intramolecular atomic orbitals, with the surface orbitals, is also very important. This can be seen most readily by analysing the bond-order overlap populations, which measure the contribution of each level of the adsorbate–surface complex with respect to its (positive or negative) contribution to the chemisorptive bond. One such bond-order overlap population curve is shown in figure 3 for the interaction of the CO 5σ HOMO orbital with the clusters. Note that this interaction specifically leads to occupied bonding as well as antibonding surface–adsorbate orbital fragments. The population of antibonding orbitals increases with coordination number. The total orbital overlap populations are presented in figure 2*b*.

The total CO 5σ fractional orbital occupation decreases with coordination number, corresponding to an adsorbate-to-substrate donative interaction. The donative interaction will usually be weak or, when the antibonding orbitals are nearly completely occupied, may even become repulsive (hollow coordination). An increase in the d-valence electron occupation would also enhance the repulsive nature of the donative interaction. For a detailed explanation of these chemical bonding features we refer to (van Santen & de Koster 1991; van Santen *et al.* 1990; van Santen & Zonnevylle 1992; Zonnevylle & Van Santen 1992).

Several important effects resulting from the choice of clusters are illustrated in figure 2*c* and table 1*a*–*c*. The interaction energies given in table 1*a* show significant changes with CO site for the 7–11 Co atom clusters. The variations between clusters in the total interaction energy are mainly due to differences in the indirect response of the clusters to the disturbance caused by the interacting CO molecule, rather than to the formation of the chemisorptive bond directly (table 1*b*). This effect can be ascribed to the differences in the net decreases in metal–metal bond strengths upon CO adsorption (table 1*c*). In contrast to the total interaction energy the overlap populations between CO and clusters are less influenced by cluster choice. The orbital overlap populations of the C–Co interaction (figure 2*c*) all indicate a stronger total interaction in atop versus bridging or hollow coordination.

As an overall result, the interaction of an adsorbed molecule changes much less with d-valence electron occupation than that of adsorbed atoms. The relative small variation of the molecule–surface interaction results from the fact that when the *d*-valence electron occupation increases, the increasing backdonative interaction is counteracted by a simultaneous decreasing donative interaction.

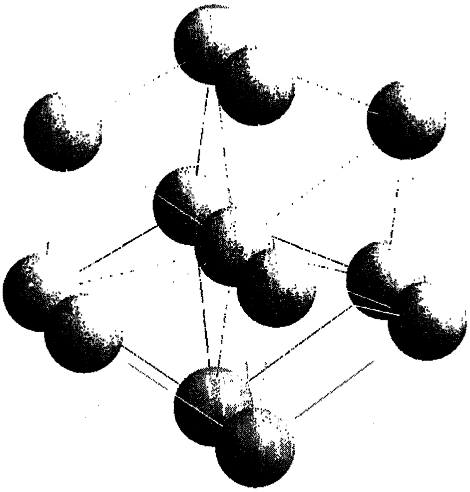

Table 1. (*a*) *Comparison of* CO *interaction energies* (kJ mol^{-1}) *as a function of* CO *coordination number computed for clusters 2c, with* CO *interaction energies computed for adsorption to the 13* Co *atom clusters* (*van Santen & Zonnevylle 1992*)

cluster size	13	9–11	7–8
onefold	−160	−200	−127
twofold	−140	−263	−218
threefold	−120	−241	−210

Table 1. (*b*) *Metal–metal atom bond weakening in the differently sized clusters, measured as percent change in bond order overlap*

(The situation of one-fold coordination is compared (van Santen & Zonnevylle 1992).)

cluster size	13	10	7
bond order overlap population change	−60	−32	−11

Table 1. (*c*) *Average* Co *metal–metal atom bond energy for clusters considered in* (*b*), *without* CO *adsorbed* (kJ mol^{-1}) (*van Santen & Zonnevylle 1992*)

bulk	13	10	7
71	100	111	140

For atoms such as C and O, however, there is only a significant change in the interaction with 2p atomic valence orbitals. The doubly occupied 2s atomic orbitals have a very low energy and their interaction is always repulsive). When the d-valence electron occupation increases, the interaction with the 2p atomic orbitals decreases because of the increased occupation of antibonding adsorbate–surface fragment orbitals.

The difference between molecular and atomic adsorption phenomenon is illustrated by the ASED calculation results presented in figure 4 (van Santen *et al.* 1990). The reaction paths illustrated in figure 4 are explained in the next section. By varying the

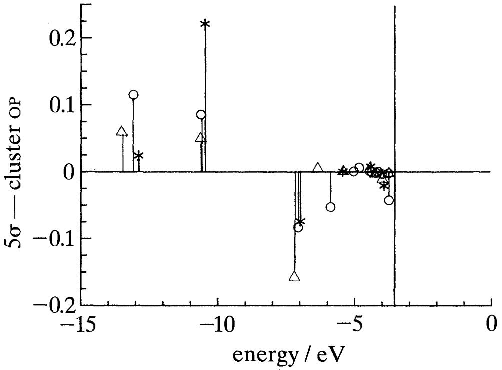

Figure 3. CO 5σ-surface orbital population as a function of energy on the same clusters as used in figure 2 as a function of position. The orbital population is positive when an orbital fragment is bonding and negative for the antibonding case. Note the minimum of energy of −12.5 eV of the bonding interaction contribution (van Santen & Zonnevylle 1992). *, Top 1; ○, bridge 1; △, hollow 1.

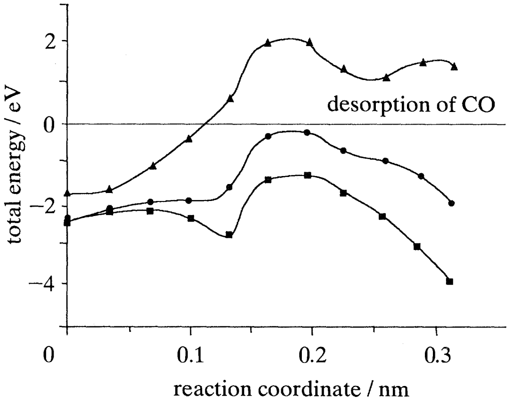

Figure 4. Change in ASED interaction energy of a dissociating CO molecule on the Rh (111) surface (19). The reaction coordinate is the projection of the CO distance on the surface. The calculations have been done for the minimum reaction energy path, to be discussed in §3*b* as determined for Rh (de Koster & van Santen 1990). ▲ denotes result for the same cluster with 1 electron per metal added (Pd). ● denotes result for the cluster with 1 electron per metal subtracted (Pd).

d-valence electron count (keeping the atomic parameters fixed), this semi-empirical method is well suited for tracing the effects of moving across the transition-metal series. As the d-electron occupation increases, the CO adsorption energy drops much less significantly than the C and O adsorption energies do. Although back-donative (M:CO) and donative (CO:M) effects change dramatically across the series, for the molecular adsorbate, the net effect remains in balance. Atomic adsorbates experience only an increasing donative, and thus increasingly repulsive, effect across the series.

(*b*) *The role of orbital symmetry*

The interaction of the adsorbed atom or molecule with the s, p-valence electron band usually dominates over that with the d-valence electrons. This is because the metal s, p-atomic orbitals are spatially more extended than the d-atomic orbitals. However, their interaction is more or less constant across the transition-metal series. The spatial extension of the d-atomic orbitals tends to increase from the right to the

Table 2. *Overlap population of the* $NH_3\sigma$ *orbital with selected copper orbitals* (*in arbitrary units*) (*Biemol et al. 1992*)

copper orbital	Cu(9, 4, 5)	Cu(8, 6, 2)
3d	−0.005	0.157
4s	0.693	0.372
4p	0.572	0.727
total	1.260	0.942

left across the transition-metal series as well as when moving downward along a column in the periodic system. This reflects in an increasing importance of the interaction with the d-valence electrons. For either molecular or atomic adsorbates, the grouping of adsorbate orbitals as either symmetric (s) or asymmetric (p) with respect to the surface normal, which we will choose along the z direction, aids the analysis.

When adsorbed to a single surface atom, by far the dominant interaction is with the metal atomic orbitals of the same symmetry. When adsorbed in higher coordination, one has to construct group-orbitals (van Santen 1987; Zonnevylle *et al.* 1989) for the surface atoms, i.e. linear combinations of nearest-neighbour metal-atomic orbitals, with coefficients given by the irreducible representation corresponding to the local symmetry of the adsorption site.

Whereas the p_x, p_y ad-atom orbitals cannot interact with the metal-atom s-atomic orbitals when adsorbed to a single surface-atom, in high coordination sites a strong interaction becomes possible with the corresponding s-atomic group-orbitals of p symmetry. Because the interaction with the s-valence electrons contributes significantly to the chemical bond strength, this causes adatoms to favour high coordination sites.

For molecules the same holds for the interaction with p-symmetric molecular orbitals, which are usually the LUMOS. So the interaction with LUMOS usually favours high coordination sites. This result was illustrated for the CO $2\pi^*$ orbital interaction in figure 2*a*. The HOMOS of the adsorbed molecule are often s-symmetric with respect to the surface normal. The relative energy of the screened HOMO-energy with respect to the s-valence-electron bond will determine, whether high or low coordination is favoured. For instance, the CH_3 fragment, with its main bonding contribution due to the σ-lone pair interaction (and little contribution from the LUMO) is found in high coordination sites on the Ni(111) surface (Schule *et al.* 1988). Ammonia, also mainly binding by way of its σ-lone pair orbital, will also favour high coordination on Ni (32). However, when interacting with a metal with a lower workfunction such as Cu, it favours low coordination sites. Whereas the interaction with the Cu 4p atomic orbitals increases with coordination number, it decreases for interaction with the Cu 4s as well as 3d atomic orbitals (see table 2).

As is shown in figure 5, for clusters modelling the (100) surface and using the LDA method, the low energy of the ammonia σ orbital results in a significant population of antibonding orbitals. For a full analysis of this feature in terms of grouporbital interactions we refer to (van Santen & Baerends 1991).

A repulsive interaction between the doubly occupied σ-NH_3 orbital and the doubly occupied d-valence electrons exists (see table 2). This repulsive interaction is proportional to the number of coordinating atoms and hence is less for low coordination. Generally one finds that the s-symmetric interaction of adsorbate

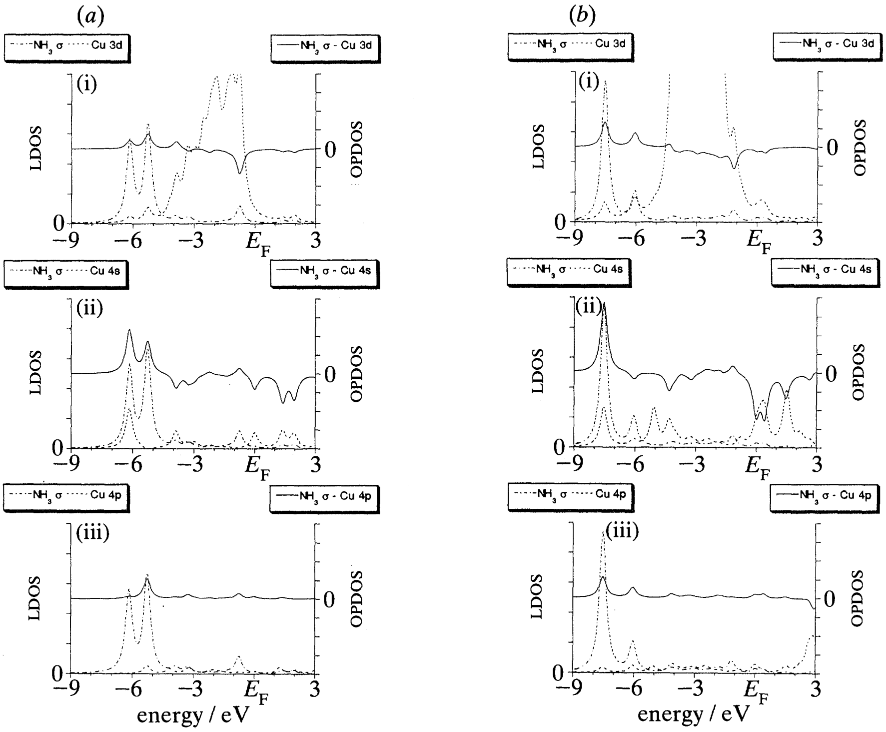

Figure 5. (*a*) One-fold coordinated NH_3 bonded to a (100)-surface type cluster. Local density of states (LDOS) of the NH_3 σ-orbital before adsorption, and the central copper 3d (i), 4s (ii) and 4p (iii) orbitals together with the overlap population density of states (OPDOS) between both the (100) surface cluster and NH_3. Zero energy in these figures corresponds to the Fermi level (E_F) (Biemolt *et al.* 1992). (*b*) Two-fold coordinated NH_3 bonded to a (100)-surface type cluster (Biemolt *et al.* 1992). LDOS of the NH_3 σ-orbital before adsorption, and the central copper 3s (i), 4s (ii) and 4p (iii) orbitals together with the OPDOS between both the (100) surface cluster and NH_3. Zero energy in these figures corresponds to the Fermi level E_F. LDOS and OPDOS are both in arbitrary units.

HOMO with the highly occupied d-valence electron band directs adsorbate molecules to low coordination sites.

The CH_3 fragment adsorbed to the Pt-surface has been predicted to adsorb atop of a Pt atom, due to the strong interaction with the spatially extended Pt 5d-atomic orbitals (van Santen *et al.* 1990).

The adsorption energy of a molecule is controlled by the balance of donating and back-donating terms. Back donation is relatively unimportant for CH_3 and NH_3 because of the high energy of their LUMOs. Back donation involving the LUMOS usually favours high coordination, donation involving the HOMOS can favour low coordination. The interaction with the d-valence-electron interaction controls the balance.

3. Dissociation and association reactions

(*a*) *The role of backdonation*

For dissociation, a molecular bond has to stretch. Assuming the molecular fragments thus generated remain adsorbed to the surface, the optimum configuration for the dissociating bond is parallel to the surface.

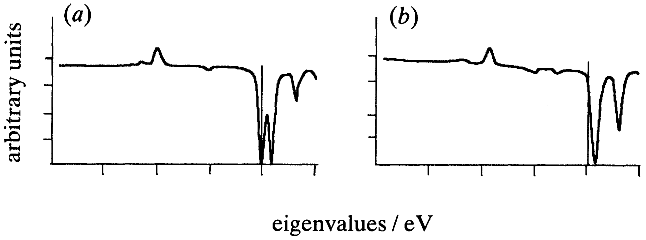

Figure 6. The changes in O–Ag overlap population of O adsorbed to a Ag_4 cluster, with O fourfold coordinated (Ag_4O) (*a*). With four additional oxygen atoms coordinated (*b*). Note the shift downwards of the antibonding AgO electron density when the oxygen concentration increases (van den Hoek *et al.* 1989).

Some molecules such as O_2 usually adsorb parallel to the metal surface (Upton *et al.* 1988; Kiskinova 1992), whereas others such as CO and NO (Kiskinova 1992) usually prefer perpendical adsorption with the carbon or nitrogen atom directed towards the surface. A molecule initially perpendicularly adsorbed has to bend before it will dissociate.

The back donating interaction between metal surface and p-symmetric antibonding LUMOs lowers the energy required of bond stretching. We have seen in §2 that the molecular LUMOs get a finite electron density. This causes weakening of the intramolecular bond, because of the antibonding nature of the molecule LUMOs with respect to the intra-molecular bond. For a diatomic molecule, adsorption parallel to the surface enables contact of two molecular atoms with the metal surface, which will favour the backdonating interaction with a LUMO, given surface group orbitals of proper symmetry are available.

However, when the d-valence electron occupation is high, interaction between the doubly occupied HOMOs of the molecule and the d-valence electrons is mainly repulsive. This tends to favour low coordination and minimal contact with the surface. It may even be the cause which forces diatomic molecules to adopt a perpendicular orientation with respect to the surface plane (Sanchez Marcos *et al.* 1990) in some instance.

If coordination is parallel to the surface the HOMO repulsive interaction with metal d-atomic orbitals may become overcome by shifting to a twofold coordination site where rehybridization of molecular HOMOs and LUMOs can occur (Sautet & Paul 1991; Chan *et al.* 1992).

Back donation is very strong on surfaces with low workfunctions and when a molecule has a high electron affinity. Then parallel adsorption may become the minimum energy configuration and high coordination sites are preferred.

(*b*) *Surface reaction paths*

Reaction paths that favour electron population of LUMOs of the dissociating molecule, as well as the development of a strong bonding interaction between the product fragments and the surface will tend to have a lower activation energy. We have already discussed that atoms and molecular fragments usually prefer bonding in high coordination sites. In addition, the product fragments should not be destabilized because of an unfavourable location with respect to each other on the metal surface. Such a destabilizing effect occurs when adatoms share a surface atom for bonding (see figure 6). So for the dissociation reaction an ensemble of accessible surface metal atoms is required.

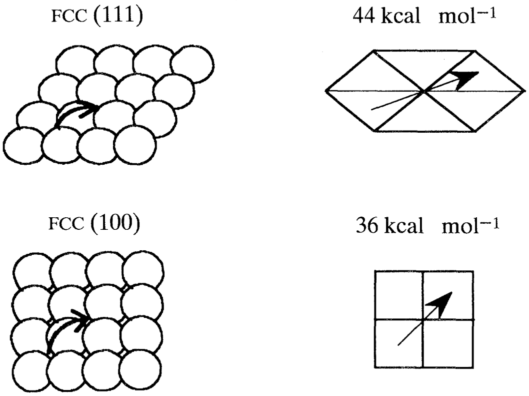

Figure 7. Minimum dissociation energy paths of CO (13) on large clusters of Rh according to the ASED method. The activation energy on the (111) surface is predicted to be 8 kcal mol^{-1} higher than on the (100) surface (de Koster & van Santen 1990). (1 cal $\approx$ 4.184 J.)

Several factors may contribute to such unfavourable interactions. On purely electrostatic grounds the direct interaction of negatively charged adatoms is unfavourable. Also, any metal adatom bond will weaken when that surface metal atom must also bind a second adatom. The effect of the latter stems primarily from the more restricted role that the s-surface metal atomic orbitals can play. The increased coordination of the metal atom with other atoms weakens the bonding interaction of the s-atomic orbital with each of the individual atoms. In essence, s-atomic electron density becomes localized in the chemical bond with the adatom. Hence less *s*-atomic electron density becomes available for other chemical bonds. For identical covalent bonds, the attractive contribution to the bond strength decreases approximately as $N^{-\frac{1}{2}}$ per bond (Cyrot-Lackman *et al.* 1974; Haydock *et al.* 1975; van Santen & Baerends 1991). (N is the number of next nearest-neighbour atoms of the central atom.)

This effect can be viewed as a consequence of the principle of bond order conservation (Shustorovich 1990), which gives as a general rule that the larger the number of bonds to a particular atom the weaker the strength per bond. Hence adatoms tend to share the least number of surface atoms as the surface coverage increases (Kiskinova 1991). It appears that the reaction paths for dissociation and association we have studied so far by theoretical means all seem to satisfy this principle of least sharing of surface-metal atoms.

Figure 7 illustrate the minimum energy paths found for CO dissociation (de Koster & van Santen 1990) on Rh (111) and Rh (100) according to the ASED method. It corresponds to the energy reaction coordinate dependence presented in figure 1. The reaction coordinate used is the projection of the CO distance into the surface plane. The threefold coordinated CO molecule starts to bend, then the oxygen end crosses a surface atom optimizing the interaction with the CO $2\pi^*$ orbital and the dissociated atoms finish in positions of optimum coordination, where they share the least number of surface atoms.

The higher reactivity of the (100) surface is due to the lower coordination of the surface-atoms. This decreases delocalization of the surface atomic electron density and hence enhances the covalent interaction with adatoms (van Santen 1987), stabilizing the products. Using the same approach we also studied the association

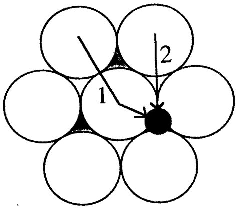

Figure 8. Recombination of CO and CH_2 with a C atom adsorbed to the Rh (111) surface (Koerts & van Santen 1991). The reaction paths show the C–C bond formation. The activation energies are, for $CH_2 + C$, 41 kJ mol^{-1} (path 1) and 50 kJ mol^{-1} (path 2). For $CO + C$ they are 121 kJ mol^{-1} (path 1) and 156 kJ mol^{-1} (path 2).

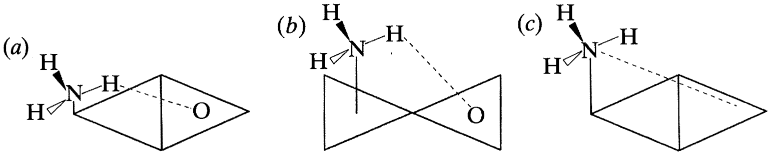

Figure 9. NH_3 oxidation on a Cu surface (Kerkhof *et al.* 1992). (*a*) No surface atom sharing reaction path between adsorbates. (*b*) One atom sharing reaction path between adsorbates. ΔH is the overall energy change of the reactions and is (*a*) 48 kJ mol^{-1}, (*b*) 48 kJ mol^{-1}, (*c*), 176 kJ mol^{-1}. E_{barr} is the maximum energy to be overcome and is (*a*) 131 kJ mol^{-1}, (*b*) 173 kJ mol^{-1}, (*c*) 344 kJ mol^{-1}.

reaction of an adsorbed carbon atom with adsorbed CH_2 and CO species, again for a Rh (111) surface (Koerts & van Santen 1991). As illustrated in figure 8, two paths were compared. In both cases the C atom starts in threefold coordination. The CH_2 fragment can approach the carbon atom by moving over one metal atom or a metal-metal bond.

In the first case one atom is shared in the transition state, in the second case two metal atoms. A significant amount of the activation energy is found to be due to the geometric necessity of the two approaching fragments to share a surface atom. The path that corresponds to sharing the least number of metal atoms is favoured.

Work by Blyholder (Blyholder & Lawless 1989) on surface-formyl formation from H and CO and Whitten (Yang & Whitten 1989, 1991), who uses first principle cluster calculations on the hydrogen addition to a chemisorbed CH_x species, gives results in line with the above conclusions. A final example concerns the dissociation of NH_3 by coadsorbed oxygen atoms on a Cu-cluster (Kerkhof *et al.* 1992). LDA calculations have been done for the different geometries denoted in figure 9. The reaction to be studied is

$$NH_3 + O \rightarrow NH_2 + OH.$$

The four species are adsorbed to a cluster simulating the Cu (111) surface. Dissociation is studied starting with NH_3 being adsorbed in top or threefold coordination at the same distance from the adsorbed oxygen atom. During hydrogen transfer the NH_3 and adsorbed oxygen atom never share a bond with a surface-atom when following reaction path *a*. Following reaction path *b* the NH_3 molecule and oxygen do share one surface atom. One finds that the least sharing atom reaction path has a significantly lower activation energy.

4. Conclusion

The following general rules are found to apply to chemisorption.

1. The adsorption energy decreases with increasing d-valence-electron band occupation for the group VIII transition metals.

2. The adsorption energy of a molecule is controlled by the balance of donating and backdonating terms; backdonation favours high coordination, donation can favour low coordination. The d-valence-electron interaction determines the balance.

3. Atoms usually favour high coordination. The adsorption energy decreases more strongly with d-valence-electron occupation than that of an adsorbed molecule.

For dissociation and association reactions only a few reaction paths with a low activation energy are available. For dissociative reactions, the availability of asymmetric surface-group orbitals suitable for backdonative interactions with unoccupied antibonding molecular orbitals is important. For association reactions a donative interaction which will withdraw electrons from antibonding orbitals forming between the fragments in the course of the reaction is more suitable.

A stable final configuration for the molecular fragments or atoms generated upon dissociation requires a reaction path proceeding on an ensemble of atoms, such that high coordination of the adsorbed dissociation products is possible. A large ensemble is also necessary so that reaction proceeds according to the minimum atom sharing principle.

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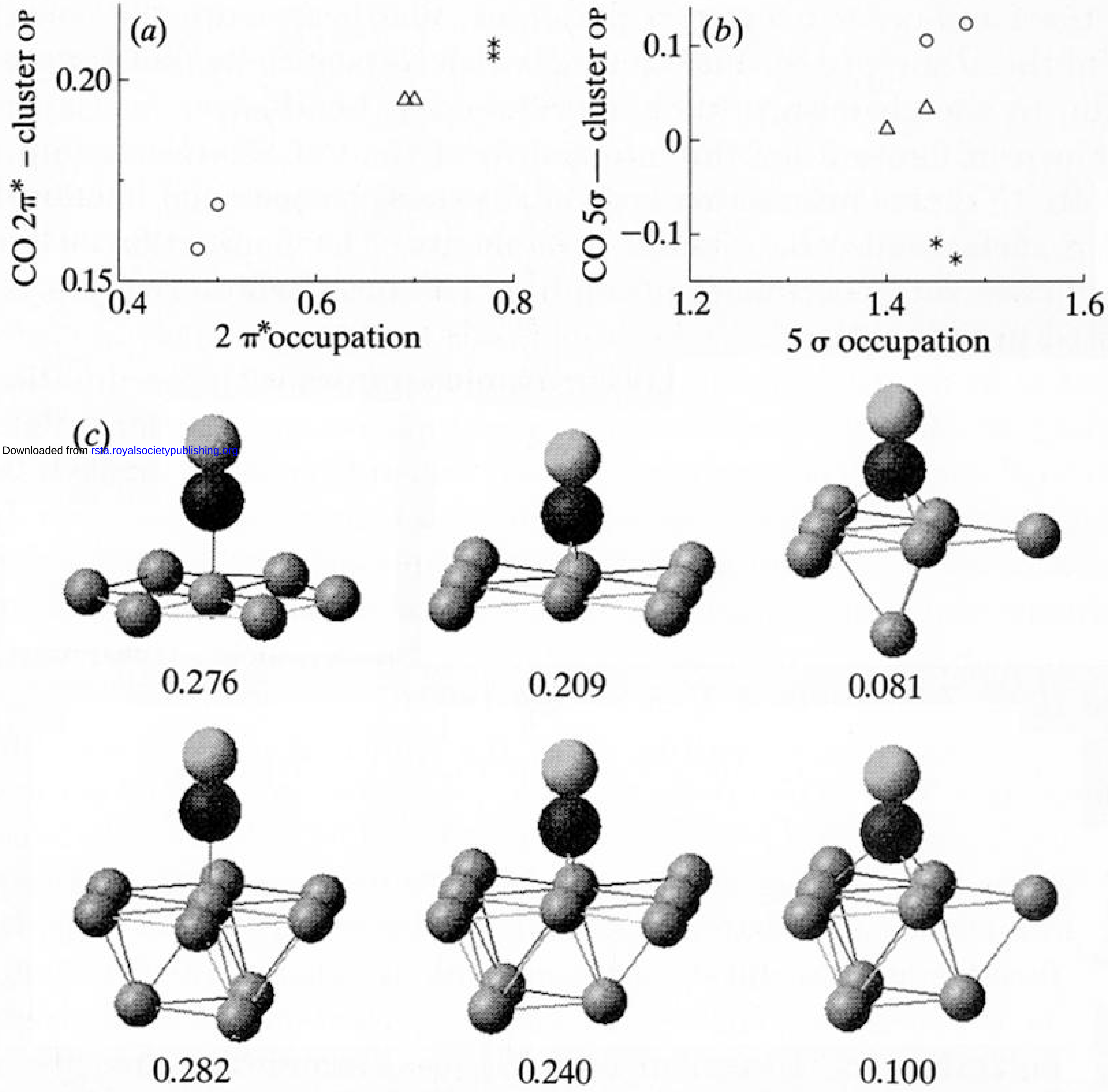
Discussion

P. C. H. MITCHELL (*Department of Chemistry, University of Reading, U.K.*). We need to be able to validate our models of surface-bound species in catalysed reactions, for example carbon monoxide in the Fischer–Tropsch catalysis. One problem is to know whether surface structures revealed by low energy electron diffraction, for example, are participants in the catalysed reaction, or merely spectators. Here the computational approach would be to calculate the structures and reactivities of candidate surface species to guess the most probable one. We must surely start with candidates known to us from molecular chemistry. An equally important problem is to be able to validate one's computational method against species with known structures and properties (not postulated surface species). Carbonyl clusters provide a wealth of structures for computational modelling studies. Our aim in computational studies should be not only to explain observed trends but more in *delimiting possibilities*. As to whether computation is relevant, we shall only know when it has been done.

A. M. Stoneham (*Harwell Laboratory, Didcot, U.K.*): Your cluster calculations appear to be a constant electron number. But if they represent a bulk solid, they should be at constant Fermi energy (this can make a significant difference when small energy levels are involved). But if they are for such small clusters, there won't be a Fermi surface to establish Friedell oscillations, and I wonder how representative of real clusters your one was?

R. A. van Santen. The cluster calculation for CO on Co and NH_3 on Cu have been done using the Amsterdam local density approximation code. This method gives chemically relevant predictions of bond energies as well as electron-energy distributions.

In most cases the clusters have been chosen to represent geometrically a part of a metal surface. They have not been chosen to give the minimum energy configuration for the particular cluster size studied. The Friedel oscillations refer to changes in the electron-energy distribution as a response to a disturbance. In a free-electron gas it is determined by the Fermi momentum at the Fermi surface. In a discrete solid there is also a dependence on the atom–atom distance. In the clusters there appears to be a change in the electron-energy distribution function (measured from the orbital overlap population) that has the same origin as the Friedel oscillation. If one were to adapt the Fermi level in cluster calculations to that of the bulk it implies charging of the clusters. This can be done, but makes comparison with surfaces even more difficult. Clearly one has to be very careful to extrapolate from results obtained by cluster calculations to surfaces. We have discussed this issue in an analysis of the results for the CO/Co system.



igure 2. (*a*) 2π*-orbital population (OP) and 2π*-surface orbital overlap population of CO adsorbed ɔ a Co cluster as a function coordination. The cluster simulates a (111) surface (van Santen & onnevylle 1992), see also (*c*). (*b*) 5σ-orbital population and 5σ-surface orbital overlap population f CO adsorbed to a Co cluster as function of coordination. The cluster simulates a (111) surface (van anten & Zonnevylle 1992), see also (*c*). In (*a*) and (*b*): ○, top; △, bridge; *, hollow. (*c*) Clusters and eometries used in (*a*), (*b*) and figure 3. Within brackets total C–Co orbital overlap population (van anten & Zonnevylle 1992).