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Model studies of the chemisorption of hydrogen and oxygen on nickel surfaces

II. Atomic chemisorption on Ni(100)

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Atomic chemisorption of hydrogen and oxygen on the Ni(100) surface has been studied using an Effective Core Potential (ECP) approach described in a previous paper. Clusters of up to 50 nickel atoms have been used to model the surface. The computed chemisorption energies are 62 kcal/mol (exp. 63 kcal/mol) for hydrogen and 106 kcal/mol (exp. 115-130 kcal/mol) for oxygen. Correlating the adsorbate and the cluster-adsorbate bonds is extremely important for obtaining accceptable results, particularly for oxygen. Reasonable convergence of chemisorption energies is obtained with 40-50 cluster atoms for both hydrogen and oxygen. For hydrogen the addition of a third cluster layer stabilizes the results considerably. Both hydrogen and oxygen are adsorbed at (or close to) the four-fold hollow site. The calculated barriers for surface migration are also in good agreement with the experimental estimates. The calculated equilibrium heights above the surface are on the other hand too high compared with experiments. This disagreement is believed to be due to core-valence correlation effects, which are not incorporated in the present ECP. The cluster convergence for the height above the surface is much slower than for the chemisorption energy.

Key words: Effective core potential — Chemisorption — Adsorption — Ni surfaces

1. Introduction

The cluster model has been used by quantum chemists to treat chemisorption phenomena on transition metal surfaces for more than ten years. In spite of this development the convergence of the chemisorption energy with cluster size and the effect of electron correlation are still not known. The reason for this is simply that accurate calculations including electron correlation on sufficiently large clusters are very difficult to perform, and thus represent one of the major challenges in modern quantum chemistry. There are two main areas of theory used to treat chemisorption on transition metal surfaces. In the first area density functional methods such as X_α [1] are used; this development will not be discussed in this paper. In the second area standard molecular orbital methods such as Hartree-Fock and Configuration Interaction are employed. In an earlier paper [2], referred to as paper I here, we have developed a one-electron type effective core potential (ECP) specifically designed to study chemisorption and surface reactions. In paper I we also discussed the early development of the molecular orbital methods for treating surface problems. We will not repeat this discussion here, but just mention the methods suggested by Melius, Upton, and Goddard [3], who were the first to advocate the use of one-electron ECPs to treat the metal atoms in transition metal clusters. Hydrogen and oxygen chemisorption on nickel has since been studied using molecular orbital methods by Upton and Goddard [4], and by Bauschlicher and Bagus and coworkers [5, 6]. In these studies the Melius ECP was used.

In the present paper we will study chemisorption of atomic hydrogen and oxygen in the four-fold hollow positions on the Ni(100) surface. We will investigate the convergence of the chemisorption energy and geometry with increasing cluster size up to clusters containing 50 atoms. The diffusion process from the four-fold hollow over the bridge positions will also be discussed.

This study has several aims. The first is simply to produce reliable results for chemisorption energies on clusters of different sizes. This information is similar to that generated experimentally by molecular beam techniques for other properties than the chemisorption energies [7]. The main piece of information we are looking for is at what size of the cluster the chemisorption energy can be considered as reasonably converged. In this context it is also interesting to see if there is a simple explanation of why the cluster convergence is achieved. The second purpose of this study is to obtain a detailed understanding of the electronic factors in the chemisorption process. The way we proceed to achieve this understanding is to successively increase the complexity of our model. In the simplest case we treat the chemisorption at the SCF level with frozen $3d$ orbitals. The next level is to relax the $3d$ orbitals, and the subsequent results are then analyzed for covalency effects. Up to this stage small clusters are used and treated at the all-electron level. At the final level the metal atoms are described as one-electron ECP atoms and the correlation contribution is added. If the information concerning cluster size convergency is combined with the detailed quantitative information on the electronic effects it should, in our opinion, constitute the major ingredients in a full understanding of the chemisorption process.

Our final results for both the hydrogen and oxygen chemisorption energies, at our highest level of treatment for the largest clusters, agree very well with the best available experimental values, although for hydrogen in particular the height above the surface is too large. The reason for this disagreement is probably the neglect of core-valence correlation effects in our present method. Core-valence correlation will be incorporated into a future one-electron ECP [8].

A rather surprising picture of the chemisorption bond emerges from our study. The conventional picture of the bonding between a surface and electronegative adsorbates is that electrons are donated from the Fermi level to the adsorbate. In this picture the strength of the chemisorption bond will be critically dependent on the position of the Fermi level. Our results are not consistent with this simple interpretation since we find a fast convergence of the chemisorption energy with cluster size even though the ionization energy converges rather slowly. We have also found cases where the chemisorption energy increases even when the ionization energy increases. Instead, our results strongly suggest the importance of the overlap between the surface orbitals and the adsorbate orbitals, and consequently the importance of covalency in the bonding. Rather than arising from a direct electron jump from the cluster to the adsorbate, the negative charge on the adsorbate is a result of polarized covalent bonds with the adsorbate.

The most important result of the present study is probably the demonstration of very large correlation contributions to the chemisorption energy. These contributions are furthermore shown to be quite localizable to the adsorbate electrons and bonds. As a result of adsorbate correlation the chemisorption energy for oxygen increases from 46 kcal/mol to 111 kcal/mol on a Ni_{25} cluster. Given the above mentioned covalent picture of the chemisorption bond, it is interesting to note that the correlation effect on the covalent bonding in water is almost equally large.

Besides the work on atomic chemisorption on nickel surfaces already mentioned [3-6], there has also been a considerable amount of work on molecular chemisorption on nickel clusters [9-11], and atomic chemisorption on copper clusters [12, 13]. Many important conclusions have been reached in these studies, but we shall mention just two: Bauschlicher and Nelin [10] showed that the chemisorption energy of CO can change dramatically even when a third layer is added to the cluster, and Bagus and coworkers [11] have demonstrated that a qualitative understanding of spectroscopic effects on molecular chemisorption can be obtained using reasonably small clusters. The results by Madhavan and Whitten [12, 13], which deviate substantially from ours, have been discussed in some detail in a paper that presents our results for hydrogen and oxygen atomic chemisorption on copper clusters [14].

2. Computational details

In this paper we will describe calculations on a number of different clusters, all of which model a four-fold hollow site and its nearest surroundings on the Ni(100) surface. One of these clusters, Ni_{25}, is shown in Fig. 1 and will be referred to in the text as $Ni_{25}(12, 9, 4)$. The designation $Ni_n(n_1, n_2, \dots)$ means that there are n nickel atoms with n_1 atoms in the first layer, n_2 in the second etc. The bond distance in the clusters is taken to be the experimental bond distance of the bulk, 4.7088 a.u., and is not varied in the present calculations.

There are at least two assumptions behind the use of one-electron ECPs for transition metals in clusters. The first assumption is that the dominating atomic

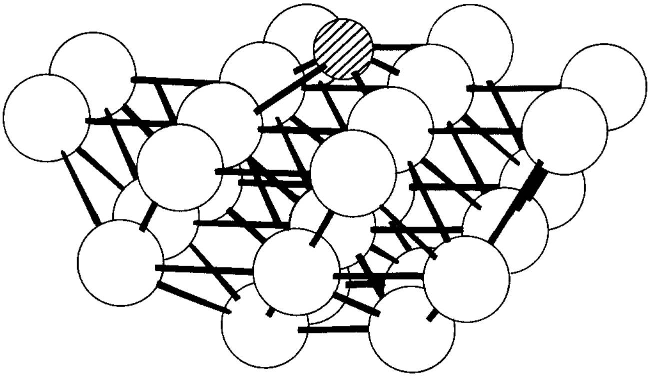

Fig. 1. The $Ni_{25}(12,9,4)+X$ system. The *large circles* denote nickel atoms, of which there are 12 in the first, 9 in the second and 4 in the third layer. The adsorbate X (*small dashed circle*) is positioned in the four-fold hollow site

state is $d^{n+1}s$. For nickel and copper this is also a low lying state for the free atom. In cases like cobalt and iron, however, the $d^n s^2$ state is the atomic ground state and the assumption of a dominating $d^{n+1}s$ state in a cluster would thus be more questionable. The second assumption for the use of one-electron ECPs is that the metal d orbitals should not participate in bonds to the adsorbate. In paper I we have shown that in the case of hydrogen and oxygen chemisorption on nickel in hollow positions this is a very good approximation. A third assumption might seem to be that there should be no atomic d relaxation and no mixing between the s and the d bands. This would mean that the one-electron ECP should mimic the all-electron results using frozen atomic d orbitals. The all-electron calculations in paper I showed, however, that the frozen d approximation has severe shortcomings. Oxygen in the four-fold hollow site of Ni(100) is not bound at the SCF level when the Ni $3d$ orbitals are frozen, but becomes bound by 42 kcal/mol when the $3d$ orbitals are allowed to relax. Models which do not account for this sizeable d orbital relaxation in a reasonable way can therefore lead to large qualitative errors for chemisorption problems; however, as a careful analysis of the wavefunction showed - using a localization procedure of the $3d$ orbitals - the $3d$ orbitals do not participate in the chemisorption bonds. In the case of oxygen on copper we have also calculated an upper bound to the contribution to the chemisorption energy from direct $3d$ orbital involvement in the covalent bonds [14]. This contribution, which is probably largely overestimated, is 4 kcal/mol at the bridge site, where the covalent contribution is certainly higher than the four-fold site. Judging from the size of the $3d$ coefficients in the bonding orbitals, the covalent contribution from the $3d$ orbitals may be slightly larger for nickel than for copper, but it is certainly still small (a few kcal/mol at most). Concerning the relaxation of the $3d$ orbitals, we have interpreted this effect as arising mainly from an exaggerated hardness of the outer part of the $3d$ orbitals in the frozen orbital case. To compensate for the action of the normal repulsive $3d$ projection operator in the outermost region of the orbital, we therefore suggested (in paper I) a modification of this operator by inserting a diffuse, slightly attractive component, so that the *d* relaxation effects are also modelled. The parameters in the projection operator were determined to fit the all-electron results for Ni_5O. It is clear that there are also charge polarization effects and, as mentioned above, some slight covalency effects, which contribute to the 3*d* relaxation energy and which are less well mimicked by the diffuse projection operator, but we believe that these effects are less important.

The present one-electron ECP is constructed from a combination of non-local explicit core orbital projection operators, a symmetric screening potential and a frozen 3*s* orbital. This ECP has been described in detail in paper I.

The molecular orbitals for the clusters and adsorbates were determined using the CASSCF method [15]. In most of the calculations this MCSCF method was used in its simplest form with only one configuration. Dynamical correlation effects were determined using the Contracted CI (CCI) method [16]. The CCI energies given in the tables all contain the Davidson correction [17] to account for the effect of unlinked clusters.

For the one-electron ECP nickel atoms closest to the adsorbate (i.e. five atoms for the four-fold hollow position) a 6*s*,1*p* uncontracted GTO basis set contracted to 4*s*,1*p* was used. Exponents and contraction coefficients are given in paper I. The set of four *s* CGTOs is used to construct a frozen 3*s* orbital, which will have sizeable coefficients only for the first two of these functions. As described in detail in paper I a 3*s** orbital with a node in the 3*s* region is also constructed. This 3*s** orbital is then deleted and not used in the CASSCF and CCI calculations. To describe the remaining nickel atoms in the cluster (i.e. in general all atoms except five), a smaller basis set consisting of four *s* GTOs contracted to two *s* was deemed sufficient. No frozen 3*s* orbital is employed for this basis set.

For hydrogen a five *s* GTO set [18] contracted to three *s* CGTOs augmented with one diffuse *s* function with exponent 0.03 and two *p* functions with exponents 0.8 and 0.2 were used in most of the chemisorption calculations. For oxygen the starting point was a 4*s*,3*p* set [19] which was then augmented with a diffuse *p* function with exponent 0.059667 and a *d* function with exponent 1.0. In a special study on Ni_5X several different basis sets for hydrogen and oxygen were tried. These basis sets will be described in Sect. 3.3, where the results of the calculations are discussed.

3. Chemisorption calculations

In this section we will describe some general aspects of the calculation of chemisorption energies using molecular orbital methods. These aspects are mainly concerned with the treatment of near degeneracy and dynamical correlation effects.

A general point which should be mentioned first is that we will define the chemisorption energy to be the energy difference between the ground states with long and short distances between the adsorbate and the cluster. This means that the total space symmetry and even the total spin of the valence electrons are allowed to change during the chemisorption process. (Space symmetry changes are also allowed in the work of Upton and Goddard [4], and by Bauschlicher et al. [5, 6, 20, 21].) The main argument for using this principle is that, from our experience, it leads to a faster convergence of the chemisorption energy with cluster size than if the spin is fixed at its lowest possible value, as was done in [5, 6, and 20, 21]. Both procedures will converge to the true chemisorption energy when the cluster size grows, and thus both will fulfill the most basic requirement. If we were to mimic adsorption on small real clusters, an ordinary molecular type principle with conservation of spin and space symmetry might perhaps be more appropriate; however, even in this case it is questionable since large nonadiabatic coupling effects are expected, particularly for the larger clusters where the separation between electronic levels is small.

3.1. Near degeneracy effects

In comparison with ordinary stable molecules, clusters will clearly have many more near degenerate low-lying states. It is also clear that the density of these states will increase as the cluster size increases and the clusters will become more metallic. Considering the cluster as an ordinary molecule one might therefore expect that the energy obtained with a single reference state CI wavefunction using SCF orbitals should be quite inadequate for the larger clusters, and strongly call for the use of MCSCF and multireference CI methods. Opposed to this trend is, however, the decrease in the size of the matrix elements between the nearly degenerate configurations as the clusters increase in size. We will show below that this latter effect dominates in cluster calculations, and actually leads to quite a reasonable one-reference state CI description of very large clusters. The fact that a coefficient of a certain size is less important for a cluster than for a stable molecule can be understood from second order perturbation theory: the energy contribution from a coefficient of a certain size is directly proportional to the excitation energy, and this excitation energy is typically at least an order of magnitude smaller for a cluster than for an ordinary stable molecule. In most of the calculations presented in this paper, the orbitals for the clusters are therefore generated at the one configuration SCF level, and only one reference state is used in the CI calculations.

As an adsorbate is added to the cluster, other near-degeneracies, which are energy-sensitive, may appear. In the present application to hydrogen and oxygen chemisorption, near degeneracy effects may range from bonding to antibonding excitations depending on the strength of the covalent surface-adsorbate bonds. To test if the single reference state CI description is sufficient for describing a chemisorption system, a few CASSCF and CCI calculations were performed for some of the smaller clusters. The first calculation which was attempted was a full valence CASSCF calculation on Ni_5O; however, for the nickel-oxygen bonds no near degeneracy effects were found. In fact, for this reason the weakly occupied orbitals did not converge to antibonding orbitals, but to oxygen $3p$ orbitals instead. We therefore conclude that the covalency between oxygen and the cluster does not give rise to any energetically dominant near-degeneracy effects in the four-fold hollow site. A second CASSCF calculation carried out on Ni_5O used an active space which only included the bonding and the antibonding cluster orbitals. Starting with the CASSCF orbitals and choosing the two CASSCF configurations as reference states, CCI calculations were then performed. A chemisorption energy of 105.2 kcal/mol and an equilibrium height above the surface of 2.05 a.u. was obtained in these calculations. If, on the other hand, one-configuration SCF orbitals were used with only one reference state in the CCI calculations, exactly the same chemisorption energy of 105.2 kcal/mol was obtained. The height above the surface decreased slightly to 2.03 a.u. Taking account of near degeneracy effects at the CASSCF level is therefore quite unimportant - at least in this case.

Earlier calculations on Ni_9O using a preliminary ECP on nickel gave exactly the same result. For the bare Ni_9 cluster the total correlation energy increased by only 5% in going from SCF orbitals and one reference state to CASSCF orbitals and more than 10 reference states. Furthermore, as will be shown below, the total effect of inclusion of cluster correlation on the chemisorption energy is very small. It should be pointed out that these facts do not mean that correlation is unimportant for the cluster binding energy. For both Ni_5 and Ni_{13} the cluster binding energy increased by more than a factor of two after inclusion of electron correlation.

A slightly different result was obtained for chemisorption in a bridge site. For the simple system Ni_2O arranged in a triangle, oxygen binds covalently to an electron in the Ni–Ni bond, and even at the equilibrium geometry this covalent bonding gives rise to a substantial near degeneracy effect at the CASSCF level. In this case a two reference state CCI treatment using the CASSCF orbitals does increase the oxygen binding energy, but only by 4 kcal/mol when compared with a one reference state CCI treatment using SCF orbitals. This is still a small effect, but is no longer negligible.

3.2. *Dynamical correlation effects*

The effect of dynamical correlation on the chemisorption energies can be very large. In Table 1 results for Ni_5O (using a preliminary ECP) are shown for different oxygen basis sets. The dynamical correlation may increase the binding

Table 1. Basis set analysis for oxygen on the Ni_5O system (a preliminary ECP was used for Ni). Energies are in kcal/mol. ΔD_e is the correlation effect on the chemisorption energy and $Q(0)$ is the charge on oxygen

	s p d f (4 3 - -)	*s p d f* (4 3 1 -)	*s p d f* (4 4 1 -)	*s p d f* (5 5 1 -)	*s p d f* (4 4 3 1)
D_e(SCF)	31.6	33.2	35.3	36.4	37.8
D_e(CCI)	80.0	92.5	96.2	97.1	104.2
ΔD_e	48.4	59.3	60.9	60.7	66.4
$Q(0)$	−1.04	−1.07	−1.10	−0.96	−1.19

energy by as much as a factor of 2.5. In fact, the size of this correlation effect (66 kcal/mol) is similar to the energy involved in forming the two bonds of H_2O (about 55 kcal/mol). This result is thus in accord with our picture, in which the bonding is predominantly covalent in nature. The two covalent bonds are, however, polarized towards the oxygen, with the charge on the oxygen in the present calculations being about −1.0. However, preliminary calculations including core-valence correlation effects indicate that the charge is significantly reduced at this level.

The lengthening of the cluster-oxygen bond, which is obtained at the CCI level, is associated with the fact that the negative charge on oxygen increases farther out from the surface, thus also increasing the correlation energy on the adsorbate.

An important simplification for the larger clusters is to correlate just the adsorbate orbitals and adsorbate bonds, thus avoiding cluster correlation; this approach was tested for Ni_5O and $Ni_{21}O$. Pure cluster orbitals are not automatically obtained in the SCF calculations, but can be generated through a localization scheme. The localization was carried out as a unitary rotation which maximized the coefficients for the adsorbate into as few orbitals as possible; the remaining orbitals are characterized as cluster orbitals. The results for Ni_5O show that avoiding cluster correlation introduces practically no error: 1.4 kcal/mol for the chemisorption energy and 0.04 a.u. for the height above the surface. For $Ni_{21}O$, which provides a more significant test case, the loss of accuracy is 1.6 kcal/mol. The avoidance of cluster correlation was also tested for several cases of hydrogen chemisorption, and the errors were found to be at most 3 kcal/mol. In the following work, the principle of avoidance of cluster correlation is used for oxygen chemisorption on the larger clusters. For hydrogen chemisorption all the electrons in symmetry A_1 were correlated, since this was cheap anyway.

There are some marked differences between the purpose of the present localization scheme and that of Madhavan and Whitten [12]. In their embedding scheme the localization is absolutely necessary and strongly affects their results, particularly at the SCF level. In our scheme there is no effect at the SCF level, and ideally there should be no effect at the correlated level either. Our aim is only to make the calculation cheaper by the localization.

3.3. Adsorbate basis sets

Since there is such a large effect on the oxygen chemisorption energy from the correlation of the oxygen electrons and the bonds, it was decided to make an extensive oxygen basis set investigation for the Ni_5O system. The results of this investigation are shown in Table 1. The ECP used throughout this basis set investigation was a preliminary ECP (FO-ECP(a) in paper I) and not the present ECP. The choice of ECP is, however, not very important in this context since the aim is to investigate oxygen related properties.

Starting out from the standard Dunning $4s3p$ set, the basis set was increased by adding diffuse s and p functions as well as polarizing d and f functions. The most striking result is probably the small change of 4 kcal/mol in the chemisorption energy when diffuse *p* functions are added. The corresponding effect on the electron affinity of oxygen is much larger: 20 kcal/mol. This is therefore another indication that it is better to view the chemisorption bond as covalent than ionic, even though the charge on the oxygen in the present calculation is about −1.0. The effect on the chemisorption energy of the polarizing *d* and *f* functions is more pronounced, in parallel with the situation for water for example.

Since the oxygen basis set effects in Table 1 should be unrelated to both the specific ECP used and to the cluster size, the numbers in the table can be used to extrapolate the large cluster results to larger basis sets. For the large cluster claculations the 4*s*,4*p*,1*d* basis is used for oxygen, which gives a binding energy that is 8.0 kcal/mol smaller than the largest 4*s*,4*p*,3*d*,1*f* set for Ni_5O. Adding 8.0 kcal/mol to the large cluster results should therefore give a reliable estimate of the result which would have been obtained using the larger basis set.

3.4. Cluster basis set

In the calculations on chemisorption in the four-fold hollow sites, the nearest five nickel atoms are described with a larger basis set than the surrounding nickel atoms. The nearest nickel atoms have a 4*s*,1*p* basis set, whereas the other nickel atoms simply have a 2*s* basis set without a frozen 3*s* orbital; this choice of basis sets was made after some preliminary calculations on oxygen chemisorption. The neglect of the *p* function on all nickel atoms except five is perhaps the most questionable part of the basis sets used, since it has been demonstrated by Bauschlicher et al. [5, 6, 20] that qualitatively wrong results may be obtained without *p* functions. If these erroneous results are simply due to adsorbate-substrate superposition errors we expect that the errors will disappear if *p* functions are used on just the nearest nickel atoms. It is, however, also known that nickel *p* functions are very important for the cluster, increasing the binding energy by a factor of two [21]. If the neglect *p* function is to give reliable chemisorption energies, the cluster binding energy must consequently stay rather constant during the chemisorption process; fortunately this seems to be the case. In a test calculation on $Ni_{13}(4,5,4)+O$ the effect of deleting the *p* function on the eight surrounding nickel atoms was only 0.2 kcal/mol out of a total chemisorption energy of 109 kcal/mol. This, perhaps fortuitously, small effect is not completely unexpected. We have already noted that cluster correlation is quite unimportant for chemisorption energies even though the cluster binding energy is strongly affected by correlation. It should be added that the description of the majority of the nickel atoms by only two *s* functions is what allows us to go to very large clusters. The largest cluster treated in this paper contains 50 atoms, but clusters with 70–80 atoms are not beyond reach using these small basis sets.

4. Hydrogen chemisorption

Atomic hydrogen chemisorption on Ni(100) was a natural first appliction of the model presented in paper I and in the previous sections. Based on the experience gained on the smaller clusters, calculations have been performed on increasingly larger clusters to test cluster size convergence. The results for the largest clusters could then finally be compared with experimental results for properties like the chemisorption energy (63 kcal/mol [22]), the equilibrium height above the surface (1.0 a.u. [23]), the vibrational frequency (597 cm^{-1} [24]) and the diffusion barrier (4 kcal/mol [25]).

The all-electron SCF results for Ni_5H after relaxing the $3d$ orbitals were 36.8 kcal/mol for the chemisorption energy (from paper I), 2.38 a.u. for the height above the surface and 835 cm^{-1} for the vibrational frequency. These results are quite well reproduced in the ECP calculations with deviations of only −3.4 kcal/mol, +0.11 a.u. and 13 cm^{-1} respectively (it should be noted that the ECP was calibrated on Ni_5O and not on Ni_5H - see paper I). Further, the charge distribution is reasonably well represented, with a charge transfer to hydrogen of 0.51 electrons compared with the all-electron result of 0.63 electrons. The $3d$ relaxation effect obtained for the chemisorption energy of 10.6 kcal/mol using the ECP at the SCF level stays nearly constant at the CCI level, 10.1 kcal/mol.

If we focus on the chemisorption energy, the most striking result in Table 2 is perhaps the small difference of 8.5 kcal/mol between the results for the smallest Ni_5 cluster and the largest Ni_{50} cluster. Actually, all the cluster results except three fall within the interval 53-63 kcal/mol. At a quantitative level, the most significant trend in the results is that there is a clear stabilization of the chemisorption energy around 60 kcal/mol for clusters with more than two layers (with only one exception - Ni_{29}). One example of the stabilizing effect of the third layer is given by the comparison between the $Ni_{17}(12,5)$ and the $Ni_{21}(12,9)$ clusters on the one hand and the $Ni_{21}(12,5,4)$ and the $Ni_{25}(12,9,4)$ clusters on the other (the only difference between these clusters is that there are 4 atoms in the third layer for the latter two clusters). The difference in chemisorption energy for the first two clusters is 9.9 kcal/mol and between the latter two clusters 4.1 kcal/mol. Two main conclusions can be drawn from these calculations: (i) on a qualitative level, significant information about the nature of the chemisorption bond can be

Table 2. Chemisorption of hydrogen in the four-fold hollow position of Ni(100). R_e is the equilibrium height above the surface and ω_e the corresponding frequency. D_e is the chemisorption energy

Cluster	R_e(CCI) a.u.	ω_e(CCI) cm^{-1}	D_e(SCF) kcal/mol	D_e(CCI) kcal/mol
$Ni_5(4,1)$	2.49	848	33.4	54.1
$Ni_{17}(12,5)$	1.66	762	42.6	52.9
$Ni_{21}(12,9)$	1.94	874	35.4	43.0
$Ni_{25}(16,9)$	1.37	625	35.3	45.2
$Ni_{37}(24,13)$	1.74	714	29.0	46.4
$Ni_{21}(12,5,4)$	2.22	846	44.0	63.0
$Ni_{25}(12,9,4)$	2.12	868	41.3	58.9
$Ni_{29}(16,9,4)$	2.12	869	38.6	53.5
$Ni_{41}(16,9,16)$	1.74	797	49.8	61.1
$Ni_{50}(16,9,16,9)$	2.11	904	42.4	61.6
Expt.	1.0	597		63

obtained from accurate studies of a small cluster like Ni_5, and (ii), quantitatively, for the fourfold hollow centred clusters, three layers are needed to reach the experimental chemisorption energy for hydrogen on the Ni(100) surface.

Another striking result in Table 2 is the importance of electron correlation. It is actually more important to include electron correlation than to go to very large clusters for obtaining a reasonable chemisorption energy. This statement is even more significant for oxygen chemisorption, as will be shown below. The nature of the relevant electron correlation is also clear when the orbital localization procedure described in Sect. 3.2 is applied. The results in Table 2 are obtained after correlation of all the electrons in the first symmetry; if only the localized orbitals with hydrogen character (generally one or two orbitals) are correlated very similar results are generated. The energy differences obtained are 3 kcal/mol or less in all cases, showing that changes in the cluster correlation energy due to chemisorption are almost insignificant. Results of similar accuracy have been obtained for hydrogen adsorbed on lithium clusters by Koutecky et al. [26] using a projection operator formalism for localizing the orbitals.

An interesting and surprising result in Table 2 is that the correlated chemisorption energies converge faster than the corresponding SCF values. This effect has to do with the fact that the correlation contribution to the chemisorption energy increases with increasing equilibrium height above the surface. This is not only due to the larger charge farther out from the surface (see the discussion in Sect. 3) but also to a weaker covalency in the bonding for clusters which adsorb with a larger equilibrium height above the surface. The weaker covalency leads to somewhat larger effects from bonding to antibonding excitations, and to smaller SCF chemisorption energies. If Ni_{41} and Ni_{50} are compared, for example, Ni_{41} has the smaller height above the surface, 1.74 a.u. compared with 2.11 a.u. for Ni_{50}, and therefore the larger SCF chemisorption energy, 49.8 kcal/mol compared with 42.4 kcal/mol. The larger height above the surface for Ni_{50} then leads to a larger correlation contribution to the chemisorption energy than is the case for Ni_{41}: 19.2 kcal/mol compared with 11.3 kcal/mol. The correlated chemisorption energies differ by only 0.5 kcal/mol.

While the convergence of the chemisorption energy with cluster size can be said to be quite reasonable, the corresponding convergence of the equilibrium height above the surface is far from satisfactory, particularly in relation to the experimental value 1.0 a.u. This is a rather surprising result and is quite different from earlier experience of cluster size convergence. In SCF calculations of hydrogen chemisorption on beryllium clusters Bagus et al. concluded that properties such as bond distance and vibrational frequency converge quite rapidly with cluster size while others, e.g. dissociation energies, converge more slowly [27]. The main reason for the poor results for the bond distance in the case of the nickel clusters is probably the neglect of core-valence correlation energy. Core-valence correlation effects are negligible for beryllium but can substantially shorten bond distances in the case of nickel compounds. In a future extension of our ECP [8], following the method of Müller et al. [28] will be used to include core-valence correlation; one version of this method has been applied to ECP's by Stoll et al.

[29]. The reason we suspect core-valence correlation effects to be responsible for our large error in the height above the surface, and not other errors in the ECP, is that we are able to reproduce the geometry of Ni_5H reasonably well from all-electron SCF calculations with our ECP. One should also remember that correcting a large error in the height above the surface of 0.5-1.0 a.u. requires a shortening of the bond distance by only 0.2-0.4 a.u.; this is only slightly more than the bond shortening obtained for NiH by correlating the $3d$ shell [30]. It is not clear, however, whether the nice agreement between theory and experiments for the chemisorption energy will be destroyed when core-valence correlation effects are added. Adding core-valence correlation has two opposite effects on the chemisorption energy of X to Ni_n. If we consider an ionic adsorbate, the diabatic dissociation would be to $X^- + Ni_n^+$, and core-valence correlation would clearly increase the dissociation energy to this asymptote. The chemisorption energy is, however, calculated with respect to dissociation to $Ni_n + X$. The difference between the neutral and the ionic asymptote will also increase when core-valence correlation is included and we thus have two opposing effects. A small total effect from core-valence correlation on the chemisorption energy is therefore not unlikely.

Several investigators have found a slow convergence of the chemisorption energy with cluster size, which is contrary to our findings in the present study. We have already mentioned the results by Bagus et al. [27] for hydrogen on beryllium clusters. A similar poor convergence was also found by Koutecky et al. [26] for hydrogen on lithium clusters, and slow convergence has also been demonstrated for on-top chemisorption of CO on both nickel clusters [10] and copper clusters [31]. Finally, Madhavan and Whitten [12] also find a poor convergence for hydrogen on copper. There could be several reasons for the different experiences of these studies and the present one. One reason is clearly that the mentioned systems are all different from the present system. Another reason could be the higher accuracy of the present study (this point concerns specifically [12]). A third reason might be that the present clusters are constructed in a different way from those of the other studies: all of our clusters are centred around the four-fold hollow site on the Ni(100) surface. Clusters centred differently, or modelling other surfaces (like the Ni(111) surface), may show another convergence pattern. This is presently under investigation. One recent study, which is similar to ours in all the above mentioned respects, is presented by Bauschlicher [32]. In the case of oxygen chemisorption in the four-fold hollow site of Ni(100) he finds a very slow convergence of the chemisorption energy with cluster size; however, this only results from using a different definition of the chemisorption energy from ours, and from a probable convergence to an excited state in his calculations (see discussion below in Sect. 4).

The vibrational frequencies were determined at the SCF level using a third degree polynomial with the outermost grid points spanning a distance of 1.0 a.u. (i.e. 1.5, 2.0, 2.5 a.u. and the equilibrium distance). The calculated frequencies are generally too high by around 2-300 cm^{-1}. For $Ni_{25}(12,9,4)$ the frequency was also obtained at the CCI level, but the frequency did not change significantly from the SCF result. It might at first sight not seem likely that core-valence correlation should correct the error in the frequency, since the general experience is that these effects will increase the frequencies slightly (as occurs, for example, with the alkali metal dimers [19]). However, in the present case we are not interested in a frequency with motion directly towards an atomic centre, but in a frequency with motion perpendicular to the surface. It is undoubtedly the projection of this motion towards the nearest metal atom that will determine the magnitude of the frequency. This projection will decrease with a decrease in the height above the surface and consequently lead to a decreased frequency. Core-valence correlation is therefore a very likely candidate for correcting both the height above the surface and the vibrational frequency. A more accurate determination of the vibrational frequencies using a denser grid might also improve the results slightly.

A sensitive test on the quality of the ECP and on the cluster size convergence is the calculated barrier for atomic diffusion. For atoms on Ni(100) this barrier is taken to be equal to the energy difference between the four-fold hollow position and the bridge position. This procedure is based on the assumption that the equilibrium position is exactly at the four-fold hollow site. We have not checked this assumption in this work but such work is presently in progress. The experimental diffusion barrier is 3.9 kcal/mol [25]. The $Ni_{25}(12,9,4)$ cluster gives the very good result of 4.8 kcal/mol for this quantity at the CCI level, which is not unexpected considering the fact that the chemisorption energy has almost converged for this cluster; the estimated error bars for the diffusion barrier are at most 2 kcal/mol. The SCF result for the diffusion barrier is 3.3 kcal/mol. The much smaller clusters we have tried did not give acceptable diffusion barriers, with the barrier for Ni_{11} being more than two times too high (10.3 kcal/mol), and the bridge position for Ni_5 being 4.0 kcal/mol too stable.

It is interesting to compare the present results for hydrogen chemisorption with those obtained by Upton and Goddard [4] using a similar ECP technique. On a $Ni_{20}(6,8,6)$ cluster (centred around a bridge position) they obtained a chemisorption energy of 70.1 kcal/mol in the four-fold site on Ni(100), a height above the surface of 0.57 a.u., a vibrational frequency of 589 cm^{-1}, and a diffusion barrier of 7.1 kcal/mol. These results were obtained without correlating the adsorbate. Our SCF result for Ni_{20} is 47 kcal/mol, which is more than 30% less than the value obtained by Upton and Goddard, for the height above the surface is 2.07 a.u. and for the frequency 717 cm^{-1}. It is not easy to explain these large differences, but it is obvious that the procedure of optimizing a one-electron ECP on the atom certainly does not lead to unique results for cluster chemisorption. Systematic comparisons with all-electron calculations on smaller clusters followed by a recalibration of the ECP to fit these results is, in our opinion, the only workable way to obtain reliable results.

One final comment concerning the limiting chemisorption energy may be appropriate. The chemisorption energy for our largest cluster is about 62 kcal/mol, in excellent agreement with the experimental value 63 kcal/mol. This agreement is, however, partly fortuitous, since the ECP underestimates the chemisorption energy by 3 kcal/mol compared with the all-electron results on Ni_5H [2], and an additional effect of 2–4 kcal/mol is expected by further basis set extensions on

Ni in the all-electron calculations. A limiting chemisorption energy of 65–70 kcal/mol is thus expected if these corrections are accounted for. An overestimate of the chemisorption energy is conceivable in our model since the strength of the metal–metal bonds, some of which are broken in the chemisorption process, is underestimated.

5. Oxygen chemisorption

Oxygen forms two chemisorption bonds and also becomes more ionic than hydrogen on nickel surfaces, and is therefore another useful test of the accuracy of our chemisorption mode. Reliable experimental results exist for both the height above the surface, 1.63 a.u. [33], and the vibrational frequency, 430 cm^{-1} [34]. Although the four-fold position is the most generally accepted chemisorption site, it has recently been suggested that oxygen should occupy a pseudo-bridge position with a distortion from the exact four-fold position by 0.3 Å [35]. The analysis of this LEED assignment has since been questioned, and the four-fold position is again suggested to be the most stable one [36]. For the chemisorption energy there are two slightly different experimental results: a calorimetric value of 115 kcal/mol [37], and another more indirect value of 130 kcal/mol. The latter value is obtained by a combination of two experiments, a nitrogen atom desorption experiment [38] and an ESCA experiment [39] relating the chemisorption energy of nitrogen and oxygen through the equivalent core model and a Born–Haber cycle. We have discussed this experiment in detail in a recent paper, and conclude that if corrections are made for the underlying approximations in the analysis of the experiment, a value for the chemisorption energy of about 125 kcal/mol is obtained rather than 130 kcal/mol [40]. Finally, based on a 20% ratio between diffusion barrier and chemisorption energy, it is possible to estimate diffusion barrier for oxygen of 23 kcal/mol (the ratio for oxygen on Pt(111) is 19%) [41].

The ECP was calibrated against all-electron SCF results for Ni_5O (paper I), and the agreement between the two types of calculations is therefore excellent.

The correlated chemisorption energies for oxygen in Table 3 fall in the interval 96–111 kcal/mol and thus show a similar spread and convergence as the corresponding results for hydrogen. The surprisingly small difference between the smallest and the largest cluster results for hydrogen is actually even more pronounced for oxygen. One difference between the hydrogen and the oxygen results, however, is that the considerable stabilization found for hydrogen after the addition of the third layer is not present for oxygen. The calculated result for the oxygen chemisorption energy for our largest cluster, Ni_{41}, of 106 kcal/mol is quite consistent with the experimental values of 115–130 kcal/mol. In Table 1 and in the discussion in Sect. 3.3 we showed that at least 8.0 kcal/mol should be added to the calculated chemisorption energy to correct for basis set deficiencies on oxygen (additional *d* and *f* functions). Our best theoretical estimate is thus 114 kcal/mol.

For an ionic adsorbate like oxygen, the chemisorption energy may be expected to increase as the cluster ionization energy decreases. No such relationship is found, however. For example, a comparison of Ni_5 and Ni_{29} shows that Ni_5 has

Table 3. Chemisorption of oxygen in the four-fold hollow position of Ni(100). R_e is the equilibrium height above the surface and ω_e the corresponding frequency. D_e is the chemisorption energy

Cluster	R_e(CCI) a.u.	ω_e(CCI) cm^{-1}	D_e(SCF) kcal/mol	D_e(CCI) kcal/mol
Ni_5(4,1)	2.03	323	42.9	105.2
Ni_{13}(4,5,4)	(2.00)	—	49.9	109.0
Ni_{21}(12,9)	1.85	368	51.2	111.3
Ni_{25}(16,9)	(2.00)	—	44.5	—
Ni_{25}(12,9,4)	1.93	475	45.9	111.0
Ni_{29}(16,9,4)	1.97	486	35.3	96.3
Ni_{41}(16,9,16)	2.04	390	50.0	106.1
Expt.	1.63	430		115-130

a larger chemisorption energy by 9 kcal/mol but also a larger ionization energy by 0.3 eV.

The importance of correlating the adsorbate is very pronounced for oxygen chemisorption, with the chemisorption energy at the CCI level being a factor of 2.5 greater than the SCF result. The reason for the large effect of electron correlation is that two covalent bonds are formed simultaneously, and also that oxygen becomes negative, with a charge of about −1. The correlation effect, 65 kcal/mol, is consequently larger than the corresponding effect of 55 kcal/mol in H_2O, and much larger than the correlation effect on the oxygen electron affinity of 44 kcal/mol. As for hydrogen there is also a tendency for the CCI chemisorption energies to converge faster than the SCF values, even if this tendency is not as pronounced for oxygen.

The calculated height above the surface of around 2.0 a.u. is much larger than the experimental value of 1.63 a.u. This was expected in light of the results obtained for hydrogen. Again, we expect that a proper inclusion of core-valence correlation effects will correct the major part of this error.

The results for the vibrational frequency, 475 cm^{-1} for Ni_{25} and 390 cm^{-1} for Ni_{41}, are surprisingly close to the experimental value of 430 cm^{-1} considering the relatively large error in the calculated height above the surface. In [34] it is, however, pointed out that the phonon coupling is not negligible, and that the rigid lattice frequency (which is the proper frequency for a comparison) is only 350 cm^{-1}. One should also note that there is a smaller error in the height above the surface for oxygen than for hydrogen.

The one reference state CCI result for the barrier to oxygen migration over the bridge site for the Ni_{25} cluster is 36.5 kcal/mol using the relaxed ECP. This value is much larger than the experimental estimate of 23 kcal/mol [41], which does, however, have an uncertainty of 5-10 kcal/mol. Considering the rather uncertain experimental value, the difference between the experimental and calculated result is not alarming, but is still big enough to deserve a more careful analysis. As mentioned in Sect. 3.1 the one reference state approximation is not as good at the bridge site as it is for the four-fold hollow site. More accurate two reference state CCI calculations based on CASSCF orbitals reduced the barrier to migration down to 32 kcal/mol, which is still 9 kcal/mol larger than the experimental estimate. This difference could be due to a contribution of 3*d* bonding in the bridge site, which is not accounted for in these types of calculations. To investigate this problem, all-electron calculations on Ni_2O were performed. These calculations, however, showed that the difference is due to an underestimated 3*d* relaxation effect at the bridge site instead. The all-electron calculations gave a relaxed binding energy in Ni_2O which is 11 kcal/mol larger than was obtained in the corresponding ECP calculations (it should be pointed out that the relaxation energy per nickel atom is much larger at the bridge site than at the four-fold site). Subtracting these 11 kcal/mol a value of 21 kcal/mol is predicted for the diffusion barrier, which is fortuitously close to the experimental estimate. We believe, however, that adding minor effects calculated at the all-electron level to the large cluster ECP results is a reliable procedure. With such a large estimated diffusion barrier of 21 kcal/mol our calculations support the later experiments which assign the adsorbtion site at the four-fold hollow position [35], at least in the low coverage limit.

The presently calculated results for oxygen chemisorption can be compared with two earlier similar calculations [4, 32] both using the Melius ECP [3]. For their $Ni_{20}(6,8,6)$ cluster in the four-fold hollow position Upton and Goddard [4] obtained a chemisorption energy of 83.7 kcal/mol, a height above the surface of 1.04 a.u. and a vibrational frequency of 218 cm^{-1}. These results, obtained at the SCF level, show no resemblance to our SCF values. Not enough details are given in [4] to fully understand the discrepancy between our results and theirs. Recently, however, Bauschlicher [32] published a study of the effect of cluster size on oxygen chemisorption on Ni(100) also using the Melius ECP but with larger valence basis sets than those used by Upton and Goddard. Two different clusters were used, a $Ni_{25}(16,9)$ and a $Ni_{41}(16,9,16)$ cluster. The chemisorption energies obtained at the SCF level were 88.8 kcal/mol and 41.3 kcal/mol respectively. The conclusion, at variance with the conclusions in the present paper, was then that chemisorption energies converge very slowly with cluster size. However, one reason such poor convergence was obtained is that Bauschlicher used a different definition of the chemisorption energy from that used in this work. Our convention (see Sect. 3) is to take the energy difference between the ground state at short distance and the ground state at long distance. These two states are allowed to have both different spin and space symmetry. This was not allowed by Bauschlicher, who only considered states with the lowest possible spin quantum number; for the free Ni_{25} and Ni_{41} clusters this means doublet states. This is in agreement with what we used for Ni_{41}, but for Ni_{25} there is a lower lying quartet state which is 15 kcal/mol lower than the lowest doublet state in our calculation. We would therefore use a lower reference energy at long distance for $Ni_{25}O$ and consequently obtain a smaller chemisorption energy than Bauschlicher obtained. However, even if 15 kcal/mol is subtracted from Bauschlicher's result for $Ni_{25}O$, there is still a large difference between his chemisorption energy and the SCF values in Table 3. This is probably because Bauschlicher's doublet state at long distance ($^2A_1$ for Ni_{25}) is not the same as our lowest doublet state (^2E). When we redo the $Ni_{25}O$ calculations using our ECP and the states he has used, we obtain a binding energy of 83.5 kcal/mol, which is quite close to his result of 88.8 kcal/mol. Using the ground state energies at both short and long distance for $Ni_{25}O$ gives a chemisorption energy of only 44.5 kcal/mol at the SCF level, which is close to the other SCF results in Table 3.

6. Conclusion

Results have been presented for the chemisorption of hydrogen and oxygen atoms on successively larger cluster models in the Ni(100) surface. A fast convergence of the chemisorption energy is demonstrated in this case with essentially converged results using just 40–50 atoms. With a proper account of 3*d* relaxation effects, use of a large adsorbate basis set, and an accurate account of valence correlation effects, the calculated chemisorption energies for the larger clusters are close to the best experimental values. One surprising result in this context is the qualitative agreement been the results for our smallest cluster Ni_5 and the largest clusters; since oxygen becomes strongly negative, a slower convergence following that of the cluster ionization energies might have been expected. We interpret the fast convergence as the result of formation of a chemisorption bond of predominantly covalent character. The overlap between cluster orbitals and adsorbate orbitals is more important than an electron jump from the cluster to the adsorbate, and the charge on the adsorbate is instead of a consequence of polarized covalent bonds.

The detailed oscillations of the results for the chemisorption energy for the smaller clusters is more difficult to understand. We have already indicated that these oscillations cannot be simply explained by corresponding oscillations of the cluster ionization energy. Neither is there any correspondence between these oscillations and the density of states. A direct relation between the polarizability of the cluster and the chemisorption energy would have led to a monotonically increasing chemisorption energy, which is also not found. Instead, progress in the understanding of the cluster results seems to be found in a detailed understanding of both the ground and the excited states of the clusters. A study of this type has just started and will be presented in the near future.

In spite of the accurate reproduction of chemisorption energies by the present model, geometries are still quite poor. Since we follow a procedure where we make combined use of all electron calculations and ECP calculations, it is possible to relate this problem to core-valence correlation effects. These effects are not incorporated in the present model, but work along these lines is in progress [8]. The calculation of accurate geometries represents one of the most important remaining problems in the treatment of hydrogen and oxygen chemisorption on nickel surfaces.

References and notes

1. See for example, Messmer RP (1979) In: Rhodin TN, Ertl G (eds) The nature of the surface chemical bond. North-Holland, Amsterdam, and Kasowski RV, Rhodin T, Tsai M-H (1986) Appl Phys A41:61 and references therein

2. Panas I, Siegbahn P, Wahlgren U (1987) Chem Phys 112:325
3. Melius CF, Upton TH, Goddard WA (1978) Solid State Comm 28:501
4. Upton TH, Goddard WA (1981) CRC Critical Reviews in Solid State and Materials Sciences
5. Bauschlicher CW, Walch SP, Bagus PS, Brundle CR (1983) Phys Rev Lett 50:864
6. Bauschlicher CW, Bagus PS (1984) Phys Rev Lett 52:200
7. See for example, Smalley RE (1985) In: Bartlett RJ (ed) Comparison of *ab initio* quantum chemistry with experiment for small molecules. Reidel, Dordrecht
8. Pettersson L, Siegbahn P, Åkeby H, Wahlgren U: to be published
9. Walch SP, Goddard WA (1976) J Am Chem Soc 98:7908
10. Bauschlicher CW, Nelin CJ (1986) Chem Phys 108:275
11. Hermann K, Bagus, PS (1977) Phys Rev B16:4195; Bagus PS, Hermann K, Seel M (1981) J Vac Sci Technol 18:435; Muller W, Bagus PS (1985) J Vac Sci Technol A3:1623; Bagus PS, Muller W (1985) Chem Phys Lett 115:540
12. Madhavan PV, Whitten JL (1981) Surf Sci 112:38; ibid (1982) J Chem Phys 77:2673; Whitten JL, Pakkanen TA (1980) Phys Rev B21:4357
13. Flad J, Igel-Mann G, Dolg M, Preuss H, Stoll H (1985) Surf Sci 163:285
14. Mattsson A, Panas I, Siegbahn P, Wahlgran U, Åkeby H (1987) Phys Rev B36:7389
15. Roos BO, Taylor PR, Siegbahn PEM (1980) Chem Phys 48:157
16. Siegbahn PEM (1983) Int J Quantum Chem 23:1869.
17. Davidson ER (1974) In: Doudel R, Pullman B (eds) The world of quantum chemistry. Reidel, Dordrecht
18. Huzinaga S (1965) J Chem Phys 42:1293
19. Dunning TH (1970) J Chem Phys 53:2823
20. Siegbahn PEM, Blomberg MRA, Bauschlicher CW (1984) J Chem Phys 81:2103
21. Cox BN, Bauschlicher CW (1981) Surf Sci 108:483
22. Ertl G (1979) In: Rhodin TN, Ertl 6 (eds) The nature of the surface chemical bond, chap 5. North-Holland, Amsterdam
23. Stensgaard I, Jacobsen F (1985) Phys Rev Lett 54:711
24. Andersson S (1978) Chem Phys Lett 55:185
25. Umrigar C, Wilkins JW (1985) Phys Rev Lett 54:1551
26. Fantucci P, Bonacic-Koutecky V, Koutecky J (1986) Phys Rev B34:2777; Beckmann H-O, Koutecky J (1982) Surf Sci 120:127; Pacchioni G, Koutecky J, Beckmann H-O (1984) Surf Sci 144:602
27. Bagus PS, Schaefer HF, Bauschlicher CW (1983) J Chem Phys 78:1390
28. Muller W, Flesch J, Meyer W (1984) J Chem Phys 80:3297
29. Stoll, H, Fuentealba P, Dolg M, Flad J, Scentpaly Lv, Preuss H (1983) J Chem Phys 79:5532; Wedig U, Dolg M, Stoll H, Preuss H (1986) In: Veillard A (ed) Quantum chemistry: the challenge of transition metals and coordination chemistry. Reidel, Dordrecht
30. Blomberg MRA, Siegbahn PEM, Roos BO (1982) Mol Phys 47:127
31. Hermann K, Bagus PS, Nelin CJ (1987) Phys Rev B35:9467
32. Bauschlicher CW (1986) Chem Phys Lett 586
33. Stöhr J, Jeager R, Kendelewicz T (1982) Phys Rev Lett 49:142
34. Andersson S (1979) Surf Sci 79:385; Andersson S, Karlsson P-A, Persson M (1983) Phys Rev Lett 51:2378
35. Demuth JE, DiNardo NJ, Cargill GS (1983) Phys Rev Lett 50:1373
36. Richter H, Gerhardt U (1983) Phys Rev Lett 51:1570
37. Brennan D, Hayward DO, Trapnel BMW (1960) Proc Roy Soc London A256:81
38. Conrad H, Ertl G, Kuppers J, Latta EE (1975) Surf Sci 50:296
39. Egelhoff WF (1984) Phys Rev B29:3681
40. Panas I, Schüle J, Brandemark U, Siegbahn P, Wahlgren U: J Phys Chem, in press
41. Shustorovich E (1986) Surf Sci Reports 6:1
42. Rohlfing EA, Cox DM, Kaldor A, Johnson KH (1984) J Chem Phys 81:3846