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A comparison of the on-top dissociation of H_2 on Ni(100) and Cu(100)

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The on-top dissociations of H_2 on Ni(100) and Cu(100) are studied using a cluster approach. Correlation effects are accounted for through the use of CASSCF and CCI methods. The central metal atom is treated with all its electrons whereas the other cluster atoms are described by recently developed one electron ECP's. A molecular chemisorbed H_2 state on nickel, similar to that recently observed experimentally, was identified in the cluster calculations and also for the triatomic NiH_2. No such state was found on copper. The large differences found for the on top dissociation of H_2 on nickel and copper are attributed solely to the difference in $3d$ orbital occupation. The parallel between the on top dissociation reaction on the cluster and the dissociation on a single atom is also studied. While the neutral triatomic NiH_2 represents a qualitatively correct model in the nickel case, the negatively charged CuH_2^- is required as a model in the copper case.

Key words: Dissociation of H_2 — Ni, Cu surfaces — Cluster approach

1. Introduction

It is an experimental fact that the hydrogen molecule dissociates on nickel surfaces even at very low temperatures [1], whereas there is an activation barrier for dissociation on copper surfaces [2]. Why this qualitative difference between copper and nickel exists presents one of the most straightforward problems in the area of surface science. It should therefore be well suited to a treatment using theoretical methods. At least two simple, and different, explanations of this difference between copper and nickel have been suggested. The first explanation, as expressed by for example Shustorovich [3], relies on the fact that the hydrogen atomic chemisorption energy is smaller for copper than for nickel. For the (100) surface, which is the chosen surface in this study, the most reliable experimental numbers are 56 kcal/mol for Cu(100) [4] and 63 kcal/mol for Ni(100) [5]. In the analytic chemisorption model of Shustorovich this energy difference of 7 kcal/mol between copper and nickel enters directly as a factor of 3/2 in the activation energy, thus indicating an activation energy for copper of around 10 kcal/mol higher than nickel. A fundamental weakness of this model is, however, that it does not differentiate between dissociation sites. In the second explanation, as expressed by for example Deuss and van der Avoird [6], by us [7] and by Harris and Andersson [8], the origin of the difference between copper and nickel is in the difference in the occupation of the $3d$ shell, where copper has a full shell and nickel has one hole. In the Deuss-van der Avoird model the dissociation takes place over a bridge position and is aided in the nickel case by the two singly occupied $3d_\sigma$ orbitals, whereas in our model the dissociation takes place in an on-top position and the most important interaction is between the antibonding $H_2\,\sigma_u$ orbital and an open $3d$ orbital of the same symmetry for nickel. The similarity between the dissociation of H_2 in homogeneous and heterogenous systems is stressed in our model. In the Harris-Andersson model the $3d$ shell serves as a sink for s-electrons which reduces the repulsion in the entrance channel.

The purpose of the present investigation is to study in detail the electronic differences between the dissociation of hydrogen in the on-top position on the Ni(100) and Cu(100) surfaces. The cluster model is the same as that used previously by us in the Ni(100) case [7], but new, and more reliable, effective core potentials (ECP's) have been developed [9, 10]. These ECP's have been carefully calibrated against all-electron calcultions including $3d$ relaxation and have been shown to yield excellent chemisorption energies for atomic hydrogen and oxygen on Cu(100) and Ni(100) [10, 11]. A better understanding of correlation effects and how to accurately treat these effects has also been obtained in recent studies [9-11] and this experience is used here to present more reliable results than in [7] for the H_2 dissociation on Ni(100). This experience allows us now, for example, to use multiconfiguration self consistent field (MCSCF) methods to account only those near degeneracy effects which are of importance for the dissociation process. This was not done in [7].

A further inspiration for the present study has been the recent interesting experiments by Mårtensson et al. [12] on the dissociation of H_2 on a stepped Ni(100) surface. By packing the surface with hydrogen atoms Mårtensson et al. were able to block the dissociation of molecular hydrogen and in this way isolate a reaction intermediate which is a precursor for the dissociation reaction. This is the first time that chemisorbed H_2 has been observed on surfaces. Mårtensson et al. also showed that H_2 chemisorbs in a parallel orientation in on-top positions. This result may in fact be viewed as experimental support for the on-top dissociation of H_2 on nickel, at least on the (100) plane. One of the purposes of this study has therefore also been to obtain more information about this form of chemisorbed H_2.

Our picture of the on-top dissociation of H_2 on nickel, which involves the direct interaction between a $3d$ Ni orbital and the σ_u orbital on H_2, was actually first suggested in connection with calculations on the simple triatomic molecule NiH_2 [13]. This reaction mechanism was later tested in cluster calculations and shown to be extremely similar to the one found for NiH_2 [7]. The H_2 dissociation on nickel is consequently an example where the analogy between small molecules and surfaces has proven useful. This type of molecule-surface analogy, which used to be very popular, is otherwise usually viewed with great scepticism today, see for example the discussion in [3]. However, there has recently been a suggestion by Garcia-Prieto et al. [14] of a reaction mechanism for H_2 dissociation on copper based on results for the triatomic CuH_2 which is analogous to our parallel between the triatomic NiH_2 and nickel surface results. In that study it was shown that involvement of a ^2P $(d^{10}p)$ state of Cu greatly reduces the barrier for H_2 dissociation. A barrier as low as 29 kcal/mol was calculated leading to a bent CuH_2 ground state. A barrier of a similar size is indicated from some experiments for H_2 dissociation on copper surfaces [15]. Without the involvement of the ^2P state of Cu a much higher barrier of 90 kcal/mol has been calculated for the dissociation of H_2 for the CuH_2 system [16]. Another purpose of the present study is therefore to test whether there is a close parallel between the CuH_2 results and the results for larger clusters. Our results on CuH_2 show in fact that in this case there are large differences between the binding in the neutral triatomic system and in the cluster, while qualitative agreement is obtained if the negatively charged CuH_2^- system is considered instead. This result is understood in terms of a large difference between the electron affinities of CuH_2 compared to those of Cu and H_2 in conjunction with the presence of easily movable electrons in the cluster.

2. Computational details

The essential features of the present model for treating chemisorption are the following. Most of the metal atoms are treated as one-electron atoms with only a $4s$ electron. The $3d$ orbitals only form a potential for the valence $4s$ electrons and are not allowed to participate in the bonds to either the adsorbate or the other metal atoms. The central metal atom over which the dissociation takes place is treated differently. All the electrons of this atom are included in the calculations, and its $3d$ orbitals are allowed to mix with all other orbitals.

The model of including all the electrons on only those metal atoms which are close (shorter than 3.5 a_0) to the adsorbate is by now a well tested procedure. For the case of atomic hydrogen chemisorption in the fourfold hollow positions on Ni(100), we found a very small difference between the case where one of the nearest nickel atoms was described by all its electrons and the case where this atom was described by a one-electron ECP [7]. The same is true for the present, newly developed, one-electron ECP [9] for the fourfold hollow position, although the difference increases with shorter distances between the adsorbate and the central atom. Direct covalency effects between the $3d$ orbital and an adsorbate in a fourfold hollow position are found to be very small for nickel and copper. This is found even for carbon and nitrogen chemisorption on nickel where the bond distances are rather short [17]. In the case of oxygen on copper the $3d$ covalency contribution was estimated to be around 2% of the chemisorption energy [10]. For the case of on-top chemisorption of CO on nickel and copper the procedure of describing only the nearest metal atom by all its electrons has been carefully investigated by Bagus et al. [18]. Excellent agreement between the use of this model and the all-electron results were obtained.

The same 13 atom cluster as was used in the previous study of the on-top H_2 dissociaton on the Ni(100) surface [7] was used in the present study, see Fig. 1. This cluster has 9 atoms in the first and 4 in the second layer.

The chemisorption energy for an adsorbate on a cluster can be computed in different ways. In our previous investigations we have considered the ground state energies for both short and long distances between the adsorbate and the cluster. This means that both the space and the spin symmetry of the wavefunction are allowed to change as the adsorbate chemisorbs. This a different procedure than the one used by for example Bauschlicher [19] or Upton and Goddard [20], who only considered wavefunctions with the lowest possible spin. Rationalizations for both procedures can easily be made and both of them will of course lead to the correct result in the limit of an infinite cluster. The rationale for using our procedure was simply that a faster convergence of the chemisorption energy was obtained in the first systematic studies we did [11] with this procedure than with the one used in [19, 20].

The calculations in [11] were for hydrogen and oxygen atomic chemisorption on Ni(100), where the clusters were centered around the fourfold hollow position. Recently other classes of clusters, such as clusters centered around an on-top position and clusters mimicking the Ni(111) surface, have also been systematically studied. It turns out that our first experience, where a rather straightforward cluster convergence yielded results close to the experimental surface results using 25 atoms, does not always hold. We have, for example, found that a prerequisite

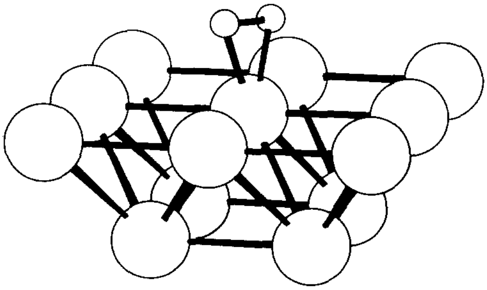

Fig. 1. The $M_{13}(9,4)+H_2$ system, where M = Ni or Cu. The *large circles* denote metal atoms, with 9 in the first and 4 in the second layer. The H_2 dissociation indicated is an on-top dissociation towards the fourfold hollow sites

for obtaining a good chemisorption energy for an adsorbate such as hydrogen or oxygen is that there is a high lying occupied orbital on the cluster of proper symmetry for interaction. A similar conclusion was also drawn by Upton and Goddard [20]. Primarily this is a requirement on the cluster, i.e. a good cluster should be such that its ground state possesses the required high lying orbitals. If this happens not to be the case, our previous experience shows that reliable chemisorption energies are obtained if the comparison is made with an excited state of the bare cluster with the proper electron configuration and corresponding states at short distances (at short distances this usually means the ground state). The arguments and the details for this procedure are given in a separate paper [21].

For hydrogen in the fourfold hollow position of a (100) surface this requirement means that a singly occupied cluster orbital of a_1 symmetry is required. In the present case of the simultaneous chemisorption of two hydrogen atoms, both a singly occupied a_1 orbital and a singly occupied b_2 orbital is required. The ground state of the M_{13} cluster has a singly occupied cluster orbital in the a_2 symmetry and does thus not meet the necessary requirements. The first cluster state which does meet the requirements appears 15 kcal/mol for Ni_{13} and 9 kcal/mol for Cu_{13} above the ground state and has open cluster orbitals of a_1, b_2 and a_2 symmetry. Nearly all chemisorption energies presented in the present study are calculated relative to this excited state of the bare cluster. The only exception is the reference state used for molecular H_2 chemisorption, see Sect. 3.1. In that case the only required excitation is from a_1 to a_2 with excitation energy 1.3 kcal/mol. The ground state was used at short distances in all cases.

An additional comment is needed to fully describe our procedure to calculate the minimal energy path for the dissociation reaction. For a cluster with an adsorbate there will always be a number of potential energy surfaces which are close in energy. It will be our assumption that the reaction at each point will take place on the potential energy surface which is at that point lowest in energy. In other words, this means that we will allow surface crossings to take place. This is a reasonable approximation if we want to model actual reactions on clusters, considering the small energy differences between the surfaces over large regions and the available coupling mechanisms such as spin-orbit interactions. If we want to model reactions on real surfaces the surface crossing model is necessary, since in this case potential energy surfaces of different local symmetry and spin lack meaning. From a more pragmatic viewpoint we have found that in the case of a more complex reaction like O_2 dissociation, staying on the same potential energy surface yields results which are completely different from results known from surface experiments. Allowing surface crossing, on the other hand, yields results which are reasonable compared with experimental results.

The central atom of the cluster is described using the SDZC set(1) basis set of Tatewaki and Huzinaga [22]. The $3d$ and $4s$ orbitals are split into two functions and a diffuse $3d$ and two $4p$-like functions are added. This is the same basis set as used in [7] and [13]. The hydrogen basis is also the same as used in [7] and [13] and is a $3s$ contraction of Huzinaga's $5s$ primitive set [23] augmented with a *p* function with exponent 0.8. In order to avoid superposition errors, the 1*s*–3*p* metal orbitals were frozen at their atomic form [24].

The surrounding (apart from the central) cluster atoms were described by our newly developed one-electron ECP's [9, 10]. These new ECP's were shown to give excellent chemisorption energies for hydrogen and oxygen in the fourfold hollow site. The relative errors were less than 10%. These ECP's, which are used in the present study, were designed to incorporate 3*d* relaxation effects through a calibration process against all-electron calculations on M_5X, with M equal Ni and Cu, and X equal H and O. Unlike the previous study in [7] no 4*p* functions were put on the surrounding metal atoms. Tests made by adding 4*p* functions yielded essentially no effect on the chemisorption energies (around 2 kcal/mol). It has previously been demonstrated (see for example [7]) that 4*p* functions on the cluster atoms can be essential for a proper description of chemisorption, and the present procedure can in fact only be safely used for hydrogen adsorbates and when the hydrogen basis set is not larger than in the present case. A test with a large 4*s*,2*p* basis on hydrogen including diffuse *s* and *p* functions gave large (around 16 kcal/mol) superposition errors when no 4*p* functions were used on the nearest metal atoms. When 4*p* functions were added on the cluster atoms the chemisorption energy dropped down to essentially the same value (within 2 kcal/mol) as that obtained without diffuse functions on hydrogen and without 4*p* functions on the metal.

Since the 3*d* orbitals, as expected, only take a minor part in the bond breaking process for $Cu_{13}H_2$, additional calculations, where the central Cu atom is described by an ECP were performed for this system as a comparison. The difference between this calculation and the one where all electrons are treated on the central Cu atom gives an estimate of the energetic importance of the Cu 3*d* orbitals for the bond breaking. A similar comparison was made in [7] for $Ni_{13}H_2$ showing the 3d orbitals were very important in this case. The basis set used for the central Cu atom in Cu_{13} in the all-ECP case included a *p* function.

The treatment of correlation effects is slightly different from in our previous study [7], where the orbitals were generated in one configuration SCF calculations. Attempts to find a small MCSCF expansion which could describe the dissociation process were unsuccessful mainly because too many configurations were needed to describe near degeneracies in the cluster. Since then, experience has been gained from the studies in [9–11] which shows that cluster near degeneracies do not need to be described at the zeroth order level as a reference for CI (configuration interaction) calculations. If, on the other hand, the near degeneracies where the adsorbate bonds are involved are included in the reference wavefunction, a large improvement in the CI wavefunction is obtained. In the previous study the poor reference wavefunction resulted in very large Davidson corrections [25] which is usually a sign of a poorly designed wavefunction. In the present case, where a preceding CASSCF [26] calculation could be performed to determine a much better reference wavefunction, the Davidson correction is much smaller and makes only a small contribution to the relative energies. In the present study the contracted CI method [27] has been used for the CI calculations. All valence electrons, including the $3d$ electrons, were correlated. Since the Davidson correction was always small we conclude that there is still no appreciable size consistency problem.

3. The on-top dissociation of H_2 on Ni(100)

The on-top dissociation of H_2 on Ni(100) towards the fourfold hollow site will proceed from one potential energy surface in the entrance channel to another potential surface (with another orbital occupation per symmetry) which defines the atomic chemisorbed state. During the reaction the wavefunction changes through three distinctly different electronic states. The first of these states, which may be characterized as molecularly chemisorbed hydrogen, represents a local minimum on the minimum energy path. The next state, which may be characterized as a dihydride state, has its minimum substantially above the curve representing two chemisorbed hydrogen atoms and does therefore not represent a true local minimum on the dissociation curve. The third state, which also represents the global minimum on the dissociation curve, corresponds to two chemisorbed hydrogen atoms. The first electronic state is in the entrance channel and is characterized by a donation from H_2 to the cluster. The H_2 bond distance is only slight elongated. This state corresponds to the chemisorbed molecular hydrogen state that has recently been observed experimentally on the stepped Ni(100) surface by Mårtensson et al. [12]. The second state has slightly negatively charged hydrogens and has a H-Ni-H angle of around 90°. This state is very similar to the dihydride molecular metal complexes obtained in homogenous processes after an oxidative addition of H_2. The H_2 bond is already broken at this stage. Finally the third state is the atomic chemisorption state. These three different states will be described in detail below in separate subsections. A schematic picture of the potential energy surface is shown in Fig. 2.

3.1. The molecular H_2 chemisorbed state

As H_2 approaches a nickel atom in a configuration parallel to the surface, the first effect on the wavefunction is a donation of charge from the H_2 σ_g orbital to the cluster. The binding energy increases from a perpendicular distance of around 4.0 a_0 between H_2 and the surface to the chemisorbed minimum at a distance of 2.84 a_0. The molecular chemisorption energy obtained at the CCI+Davidson level is 12.3 kcal/mol. Thus no barrier for forming the molecular chemisorbed state appears in calculations, and if there is a barrier in the entrance channel it must be very small. The general characteristics of the molecular chemisorbed state is given in Table 1. At the chemisorbed minimum the H_2 distance has increased from 1.41 a_0 for free H_2 to 1.69 a_0. This increase is mainly caused by the σ_g donation of 0.44 electrons but also by a back donation from the cluster to the σ_u orbital of 0.22 electrons. The total charge of H_2 is consequently +0.22. A major factor in the attraction between the surface and the H_2 molecule is the role of the $3s_\sigma$ orbital of the nickel atom. This orbital, which is singly occupied at longer distances, hybridizes efficiently with the $4s$ orbital at shorter distances and thereby reduces the closed shell repulsion between the incoming H_2 and the

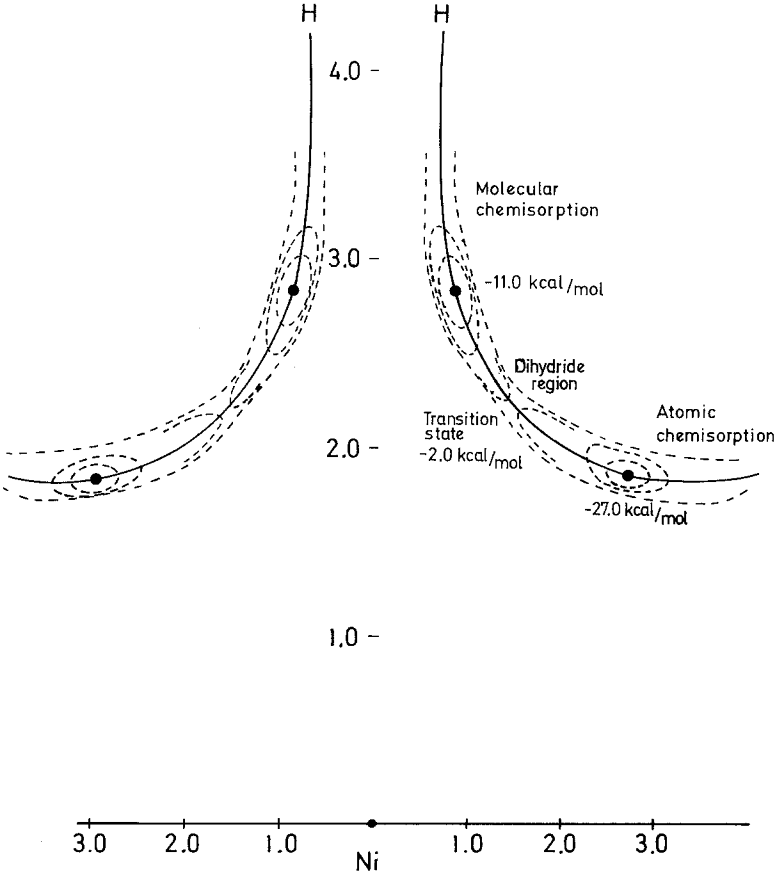

Fig. 2. A schematic picture of the potential energy surface for the on-top dissociation of H_2 on Ni_{13}. The three numbers given for the respective minima are energies with respect to H_2 at long distance from Ni_{13}. The *solid line* is the minimal energy path

surface. This hybridization effect is very important for all transition metal complexes and has been noted by us many times before [28, 29]. The two hybrids are formed through a singlet coupling between $3d_\sigma$ and $4s$ in one $(3d_\sigma + 4s)$ combination and one $(3d_\sigma - 4s)$ combination. One of these orbitals will point parallel to the H_2 axis and will gain electrons whereas the other orbital will point towards H_2 and will lose electrons as the H_2 approaches. At the minimum, the occupations are 1.88 and 0.12 respectively, compared to the long distance occupations of 1.0 and 1.0. It is very important for the efficiency of the hybridization that only two electrons are placed in these two orbitals. The reason for this is easy to understand. If only two electrons are placed in the hybridized orbitals the relative occupations of the two hybrids can change without affecting the total *d* occupation of the metal. If three electrons are put in the two hybrids any change of the relative occupations is accompanied by a corresponding change of the *d* occupation, which is expensive. Therefore, for three electrons the

Table 1. General characteristics of the molecular chemisorbed H_2 state on Ni_{13} (see Fig. 2)

a. Geometry and frequencies

$d(\mathrm{Ni}_{13}\text{-}\mathrm{H}_2) = 2.84\ a_0$, $R(\mathrm{Ni}\text{-}\mathrm{H}) = 2.96\ a_0$, $r(\mathrm{H}\text{-}\mathrm{H}) = 1.69\ a_0$

$\nu(\mathrm{H}\text{-}\mathrm{H}) = 2600\ \mathrm{cm}^{-1}$ $\nu(\mathrm{Ni}\text{-}\mathrm{H})\mathrm{sym} = 1150\ \mathrm{cm}^{-1}$

Exp. [12]: $\nu(\mathrm{H}\text{-}\mathrm{H}) = 3210\ \mathrm{cm}^{-1}$ $\nu(\mathrm{Ni}\text{-}\mathrm{H})\mathrm{sym} = 1190\ \mathrm{cm}^{-1}$

b. Orbital character

Orbital	MO-occ.	AO-occ.	Orbital character
$11a_1$	1.90	$d_\sigma(1.47)s(0.25)$	$(s-d)$ hybrid
$12a_1$	0.10	$d_\sigma(0.05)s(0.03)$	$(s+d)$ hybrid
$4b_2$	1.92	$d_{xz}(1.64)\sigma_u(0.18)$	$(d+H)$ bonding
$5b_2$	0.08	$d_{xz}(0.04)\sigma_u(0.02)$	$(d-\mathrm{H})$ antibonding

c. Total populations (all orbitals)

$q(\mathrm{H}_2) = +0.22$, $\sigma_g(\mathrm{H}_2) = 1.56$, $\sigma_u(\mathrm{H}_2) = 0.22$

$3d = 9.22$, $3d_\sigma = 1.62$, $3d_{xz} = 1.69$

hybridization has essentially disappeared and a clean d_σ orbital will become singly occupied.

The requirement of only two electrons in the two hybrid orbitals gives a constraint on the cluster valence occupation. The ground state of the bare cluster has a singly occupied cluster orbital of a_2 symmetry. The proper state for comparison must, however, have a singly occupied cluster orbital of a_1 symmetry (see the method section). The energy difference between these two states is only 1.3 kcal/mol (both states having a singly occupied d orbital of a_1 symmetry). A comparison with the ground state of the bare cluster would thus give rise to a (spurious) 1 kcal/mol barrier in the entrance channel.

It is interesting to note that in the model for H_2 dissociation proposed by Harris and Andersson [8], the reduction of the repulsion in the entrance channel through the use of the d band is also stressed. In their model, however, this reduction is accomplished by a direct transfer of electrons from the s band to the d band, whereas the main point in our model is that the sd-hybridization can occur without transferring electrons between the bands. The slight increase in $3d$-population from 9.0 to 9.2 (see Table 1) shows that the direct transfer of electrons between the bands is also present in our calculations but appears less important than the sd-hybridization.

The vibrational frequencies of the chemisorbed H_2 were measured by Mårtensson et al. using electron-energy-loss spectroscopy (EELS). The H-H stretching frequency was 3210 cm^{-1} and the Ni-H symmetric stretching frequency 1190 cm^{-1}. The H-H stretching frequency is much lower than the 4401 cm^{-1} for free H_2 [30] and this was the reason why H_2 was identified as chemisorbed rather than physisorbed. We have calculated the frequencies for the chemisorbed H_2 on the Ni_{13} cluster using a simple two dimensional parabolic fit and obtained 2600 cm^{-1} for the H-H frequency and 1150 cm^{-1} for the symmetric Ni-H frequency. There is obviously no reason to expect a perfect agreement between our values and those measured by Mårtensson et al. since the surfaces are different. Our calculated frequencies are also very approximate due to a very anharmonic surface, and changes of up to 100 cm^{-1} occurs with other selections of points for the parabolic fit. The large shift towards lower frequencies which is observed experimentally is, however, reproduced in our calculations, and we thus conclude that the same type of chemisorbed H_2 state is involved in our calculations as in the experiments. Similar chemisorbed H_2 states have recently also been observed for the molecular complex $W(CO)_3(PR_3)_2H_2$ by Kubas et al. [31]. They obtain an H-H frequency of 2694 cm^{-1}, in between the one measured by Mårtensson et al. and our value showing that this is also a chemisorbed H_2 of the same type. The complex observed by Kubas et al. has been studied theoretically by Hay [32]. Hay gave a description of the H_2 state which is quite similar to the one we have found. The bonding for this complex is also characterized by a dominating donation from the H_2 σ_g orbital to the metal, leading to a positive H_2. It is interesting to note from the work of Hay that the carbonyl groups in the metal complex have the same dissociation blocking function as the chemisorbed hydrogen layer in the surface experiments by Mårtensson et al. We interpret the larger blocking ability of the carbonyl groups compared to phosphine groups as due to a larger amount of covalent character in the carbonyl bonding.

It is interesting to compare the results for the molecular chemisorption of H_2 on the Ni_{13} cluster with the results for the same geometries of the triatomic NiH_2. The potential surface for NiH_2 indeed has a local minimum in this region corresponding to an optimal H-H distance of 1.72 a_0 and a perpendicular Ni to H_2 distance of 2.73 a_0; this is compared with 1.69 a_0 and 2.84 a_0 for $Ni_{13}H_2$. The computed frequencies are 2550 cm^{-1} for the H-H stretching frequency and 1500 cm^{-1} for the Ni-H symmetric stretching frequency, compared to 2600 cm^{-1} and 1150 cm^{-1} for $Ni_{13}H_2$. These numbers clearly show that this type of molecular chemisorbed H_2 state is characteristic of a local bonding region of H_2 to a single nickel atom. The energy for this state of NiH_2 is slightly higher, by 3 kcal/mol, than the separated ^3D nickel atom and H_2, but lower, by 4 kcal/mol, than the lowest singlet asymptote which is the ^1D state of the nickel atom. The energy for the dihydride form of NiH_2 on the other hand is still lower, by 4 kcal/mol [13], than the state which corresponds to a molecularly chemisorbed H_2.

3.2. *The dihydride type state*

As the H-H distance is increased from the minimum of the chemisorbed H_2 state described in Sect. 3.1, the energy first increases until a saddle point is reached at an H-H distance of around 2.5 a_0. The energy at this point is 2.0 kcal/mol lower than at long distance between H_2 and the cluster and does therefore not represent an actual barrier for the dissociation reaction. When the H-H distance is increased further the second, dihydride type, minimum is reached

Table 2. General characteristics of the dihydride state of $Ni_{13}H_2$ (see Fig. 2)

a. Geometry

$d(Ni_{13}\text{-}H_2) = 1.90\ a_0$, $R(\text{Ni-H}) = 3.06\ a_0$, $r(\text{H-H}) = 4.80\ a_0$

b. Orbital character

Orbital	MO-occ.	AO-occ.	Orbital character
$10a_1$	1.97	$sp(0.75)$ H(1.25)	$(sp+\mathrm{H})$ bonding
$11a_1$	1.95	$d_\sigma(1.83)s(0.02)$	$(s-d)$ hybrid
$12a_1$	0.05	$d_\sigma(0.03)s(0.00)$	$(s+d)$ hybrid
$4b_2$	1.85	$d_{xz}(1.02)\mathrm{H}(0.57)$	$(d+\mathrm{H})$ bonding
$5b_2$	0.15	$d_{xz}(0.08)\mathrm{H}(0.05)$	$(d-\mathrm{H})$ antibonding

c. Total populations (all orbitals)

$q(H_2) = -0.22$, $\mathrm{H}(a_1) = 1.34$, $\mathrm{H}(b_2) = 0.88$

$3d = 9.01$, $3d_\sigma = 1.93$, $3d_{xz} = 1.11$

on this potential surface at an H-Ni-H angle of 101° and an Ni-H distance of 3.06 a_0. The characteristics for this state are given in Table 2. H_2 is at this point bound by 7.9 kcal/mol with respect to H_2 at long distance from the surface (comparison is with the same ${}^3A_1$ state as in the molecular chemisorption case). However, another potential surface is now lower in energy at this point, with a binding energy of 20.5 kcal/mol. This is the energy surface for the atomic chemisorbed state. There is thus no true local minimum on the dissociation curve corresponding to a dihydride state.

The $3d$ orbitals of the central nickel atom play a very active role in the bond breaking process between the molecular chemisorbed minimum and the dihydride minimum. In Sect. 3.1 we mentioned that it was very important for reducing the closed shell repulsion in the entrance channel that the nickel d hole is of $d\sigma$ type in the first symmetry. Otherwise the important *sd* hybridization does not take place. For the bond breaking process it is of equal importance that the $3d$ hole moves to the second symmetry where a covalent bond to hydrogen can be formed. It is clear that all these effects - the *sd* hybridization, the motion of the d hole from the first to the second symmetry, the formation of the weak d bond in the second symmetry etc. - requires an MCSCF description which allows non integer orbital occupations. Actually five active orbitals were used in the CASSCF calculations, three in the first and two in the second symmetry. When the three most important configurations are used as reference states in the subsequent CCI calculations, the wavefunction is well behaved with a large weight for the zeroth order wavefunction. These calculations are consequently much better balanced than the previous ones from [7] and should give results of higher accuracy. The previous barrier of +4.3 kcal/mol is, for example, now reduced to a value below zero, where the reference energy is for H_2 at long distance from the cluster.

As the H-H bond is stretched from the H_2 chemisorbed minimum, the dominating mechanism becomes an electron donation into the H_2 antibonding σ_u orbital,

Table 3. General characteristics of the atomic chemisorbed state on Ni_{13} at the global energy minimum (see Fig. 2)

a. Geometry

$d(Ni_{13}\text{-}H_2) = 1.80\ a_0$, $R(Ni\text{-}H) = 3.24\ a_0$, $r(H\text{-}H) = 5.40\ a_0$

b. Total populations (all orbitals)

$q(2 \times H) = -1.11$, $H(a_1) = 1.51$, $H(b_2) = 1.60$
$3d = 9.02$, $3d_{a1} = 4.00$, $3d_{xz} = 1.02$

which eventually leads to negative hydrogen atoms with charge −0.11 at the dihydride minimum. At this point the σ_g orbital has an occupation of 1.34 and the σ_u orbital 0.88, which can be compared to 1.56 and 0.22 at the H_2 chemisorbed minimum. The $3d$ population drops slightly from 9.22 at the H_2 chemisorbed minimum to 9.01 at the dihydride minimum.

3.3. *The atomic chemisorbed state*

The geometry and total populations for the atomic chemisorbed state are given in Table 3. The wavefunction is quite different, with a different occupation in each symmetry, from the ones described in the previous subsections. The near degeneracy effects have essentially disappeared and a one configuration SCF description is therefore quite adequate as a zeroth order wavefunction. The total *d* population is close to 9.0 as in atomic nickel and the *d* orbitals do not participate in the chemisorption bonds. The hydrogen atoms become quite negative with a charge of −0.55, and the atomic chemisorption energy is 59 kcal/mol at the fourfold hollow position. The fourfold hollow position does not, however, turn out to be the most stable position for chemisorbed hydrogen on the Ni_{13} cluster. A more favourable geometry is obtained closer to the central atom: 0.63 a_0 from the fourfold position and 1.80 a_0 above the plane (corresponding to a H-Ni distance of 3.24 a_0). Since we expect the equilibrium position to shift towards the fourfold position for larger clusters it is likely that the equilibrium will eventually be at this site on the real surface. The atomic chemisorption energy at the shifted minimum for Ni_{13} is 66.5 kcal/mol, which is slightly larger than the experimental value of 63 kcal/mol [5]. A slight overestimate of the chemisorption energy may occur in our model, since the strengths of the cluster bonds, of which some are broken in the chemisorpton process, are underestimated.

Since H_2 has a calculated binding energy of 105.6 kcal/mol (experimental D_e is 109.6 kcal/mol) the exothermicity for H_2 chemisorption, as obtained for the Ni_{13} cluster, is 27 kcal/mol. The experimental exothermicity is 16 kcal/mol.

4. The on-top dissociation of H_2 on Cu(100)

The on-top dissociation of H_2 on Cu(100) was studied using exactly the same procedure as for the dissociation on Ni(100). As expected the dissociations are very different. For copper there are no states corresponding to a chemisorbed molecular state or to a dihydride state, and there is a high barrier of around 40 kcal/mol for dissociation along this dissociation path. A schematic picture of the potential energy surface for the on-top dissociation of H_2 on Cu(100) is shown in Fig. 3.

The investigation of the potential energy surface of $Cu_{13}H_2$ started with the search for a molecular chemisorbed state. Such a state was not found and the explanation is simple. It was mentioned in Sect. 3 that the hybridization between the $3d_\sigma$ and the $4s$ orbital on nickel was very important for reducing the closed shell repulsion in the entrance channel. There are two reasons why the sd-hybridization does not occur for copper. First, it is not clear that the repulsion towards the incoming H_2 will be reduced by the hybridization since one electron has to be put in the hybrid pointing towards H_2. Second, for nickel this hybridization is possible without changing the total nickel $3d$ population, but this is not possible

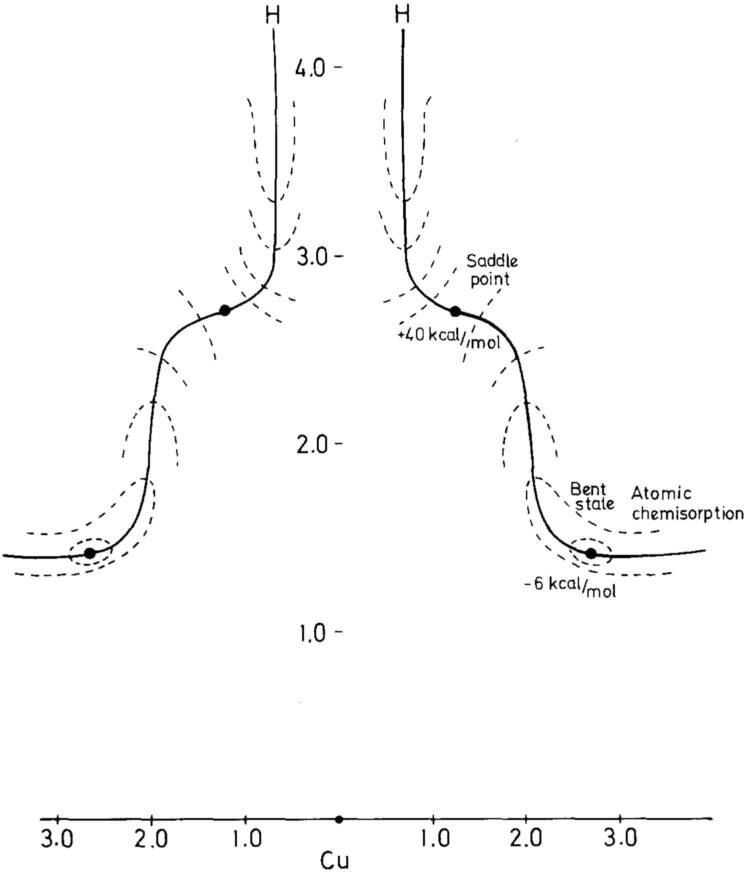

Fig. 3. A schematic picture of the potential energy surface for the on-top dissociation of H_2 on Cu_{13}. The three numbers given, for the saddle point and for the two local minima, are energies with respect to H_2 at long distance from Cu_{13}. The *solid line* is the minimal energy path

for copper. The energy gain from the hybridization is therefore compensated by the loss of energy in changing the $3d$ population.

The next state which occurred for nickel was a dihydride type state with a bond between a nickel d_π orbital and the hydrogens. No dihydride state was found for copper in the energy region of interest since copper is a d^{10} system which cannot form this type of bond with two hydrogen atoms.

Only one state thus appears in the dissociation of hydrogen on copper, namely the state which in the limit of a dissociated hydrogen corresponds to two atomic chemisorbed hydrogens (see Table 4). Similar to the case of atomic chemisorbed hydrogen on nickel the minimum energy on the dissociation curve is not found to occur at the fourfold hollow position but at a geometry where the hydrogens are displaced 0.71 a_0 towards the central atom. The atomic chemisorption energy at this point is 56 kcal/mol compared to 51 kcal/mol at the fourfold hollow position. As in the case of nickel it is not clear whether the hydrogen will chemisorb at the fourfold hollow positions or if it will become displaced towards a metal atom in the limit of very large clusters.

While the dissociation on nickel proceeds without a barrier, due to the occurrence of the two intermediate states corresponding to molecularly chemisorbed hydrogen and the dihydride, a large barrier of around 40 kcal/mol has to be passed on copper. It is interesting to compare this result with a previous study by Garcia-Prieto on the CuH_2 system for which they found a barrier to dissociation of 29 kcal/mol and a bent minimum 8 kcal/mol above the Cu and H_2 systems [14]. Our barrier is thus higher than expected from the previous study of CuH_2, and our binding energy is surprisingly large. These results prompted us to reinvestigate the CuH_2 system with our methods (of course using an all electron description of the copper atom). These calculations yielded a barrier to dissociation of 40 kcal/mol, in agreement with the barrier obtained in the cluster calculation, but a bent minimum 25 kcal/mol above the dissociation products, to be compared to a positive binding energy of 6 kcal/mol for H_2 on Cu_{13}.

While the barrier obtained in our calculations on CuH_2 agrees well with the calculated barrier for $Cu_{13}H_2$ the discrepancy in the binding energy is significant. CuH_2, of course, also has a linear minimum which is considerably more stable (by 15 kcal/mol), but this state corresponds to a d^9 configuration of the copper atom while the copper atom is in a d^{10} state in the cluster. Since for CuH_2 only

Table 4. General characteristics of the atomic chemisorbed state of $Cu_{13}H_2$ at the global energy minimum (see Fig. 2)

a. Geometry

$d(Cu_{13}\text{-}H_2) = 1.43\ a_0$, $R(Cu\text{-}H) = 3.95\ a_0$, $r(H\text{-}H) = 5.39\ a_0$

b. Total populations (all orbitals)

$q(H_2) = -0.84$, $H(a_1) = 1.44$, $H(b_2) = 1.40$
$3d = 9.92$, $3d_{xz} = 1.94$

three electrons are available for the two bonds a more appropriate comparison may be to CuH_2^-. A calculation on the negatively charged system yielded a binding energy for CuH_2^- of 3 kcal/mol relative to Cu^- and H_2 and 19 kcal/mol relative to Cu and H_2. The calculated electron affinities of CuH_2 and Cu were 44 kcal/mol and 16 kcal/mol respectively. The large electron affinity for CuH_2 is easy to understand since the added electron enters directly into one of the bonds. Since the energy cost of moving electrons within the cluster is comparatively small the large electron affinity of the CuH_2 unit thus causes a significant increase in the binding energy. The above results are compatible with a binding energy of H_2 to Cu_{13} of between 3 and 18 kcal/mol. We thus interpret the binding of H_2 as resulting from the transfer of an electron in the cluster to the central copper atom and a bond formation resembling that of CuH_2^-. The barrier to dissociation for CuH_2^- was calculated to be about 50 kcal/mol, and this quantity is thus not as affected by the presence of an extra electron as the binding energy of the bent state. This is easy to understand since the addition of an extra electron does not change the reaction from being non-allowed.

The prediction in [14] for triatomic CuH_2 differs somewhat from the results obtained in the present work. The barrier obtained in [14] is 29 kcal/mol, i.e. 11 kcal lower than ours, and the energy of the bent state is found to be only 8 kcal/mol higher than the energy of Cu and H_2. The reason for the discrepancies is most probably the particular pseudopotential used in [14], which, for example, give a different atomic spectrum than we obtain in our calculations. Most notable is that the ^2S to ^2D excitation is overestimated in [14] by 0.55 eV compared to experiment whereas we underestimate this excitation by 0.30 eV (due to the lack of *f*-functions). One reason for the problems with the pseudopotential used in [14] is that relativistic orbitals are used but the fitting is made to a non-relativistic value for the excitation energy [33]. Relativistic and non-relativistic effects are thus mixed in an uncontrollable way. A pseudopotential which properly accounts for relativistic effects should really underestimate the excitation energy by 0.5 eV [34]. This might cause problems in molecular applications. The bond distance obtained in the pseudopotential calculation also seems unreasonably short, 2.66 a_0 compared to our value 2.95 a_0.

The H_2 dissociation on Cu(100) has been studied before, using a cluster model and CI calculations, by Madhavan and Whitten [35]. They do not actually determine a transition state for the dissociation, but they estimate a barrier of 35-40 kcal/mol. This value is in good agreement with our barrier of around 40 kcal/mol. They also claim that the on-top dissociation towards fourfold hollow sites (which is the same pathway as we study in this paper), should be one of the most favorable pathways. Based on preliminary calculations for other dissociation sites we find this difficult to believe but we will return to the problem of the most favorable pathway in a coming paper. For a further discussion of the Madhavan-Whitten embedding method and a comparison to our approach, see [10].

Since we have found only small deviations from 10 electrons in the Cu 3*d* population, an interesting technical question is whether on-top dissociations on copper surfaces could also be modelled by a one electron ECP for the on-top copper atom. A similar test was made for the H_2 dissociation on-top of Ni(100) in [7] and it was demonstrated that the $3d$ orbitals need to be explicitly included in that case. For copper such an all-ECP calculation gave much more reasonable results, but there are quantitative errors. The barrier height increased from 40 kcal/mol to 60 kcal/mol and the atomic chemisorption energy at the equilibrium decreased from 56 kcal/mol to 51 kcal/mol. The all-ECP equilibrium is shifted by 0.3 a_0 from the fourfold hollow position compared to 0.71 a_0 in the all electron case. These differences consequently indicate the $3d$ orbitals also have some importance for the copper case.

5. Conclusions

The on-top dissociations of H_2 on nickel and copper are very different. On nickel there is probably no barrier. The possibility for a small barrier (~1 kcal/mol) in the entrance channel at fairly long distances from the surface can, however, not be excluded. The $Ni_{13}H_2$ calculations show two distinct minima corresponding to a molecular chemisorbed state, which is similar to a state recently observed experimentally [12], and to the atomic chemisorbed minimum. A third state corresponding to a dihydride state was also found to participate in the dissociation process. This state, however, does not give rise to any local minimum along the reaction path. The $3d$ orbitals of the on-top nickel are very active in the dissociation process, first by reducing closed shell repulsions through an *sd* hybridization in the entrance channel, and second through formation of a $3d$-bond to hydrogen in the dihydride region. Both the molecular chemisorbed state and the dihydride state are also found in the triatomic NiH_2.

The global minimum for atomic chemisorption was found for a geometry with the hydrogen displaced by 0.63 a_0 and 0.71 a_0 from the fourfold hollow position for nickel and copper, respectively. This displacement may disappear for larger clusters, although this cannot be ascertained from the present calculations.

For the on-top dissociation of H_2 on copper there is a large barrier of around 40 kcal/mol before a local minimum is reached. This minimum is similar to a corresponding minimum found for the triatomic CuH_2 [14]. The high barrier found for the on-top dissociation on copper makes it very likely that there are other pathways with lower barriers, for example dissociation over either a fourfold hollow or a bridge site. Such pathways are presently being investigated.

The explanation for the different dissociation behaviour for H_2 on nickel and on copper surfaces can at least partly be explained by the different mechanisms for the on-top dissociation. The differences for this pathway are solely due to the difference in $3d$ orbital occupation [6–8], and have nothing to do with the difference in chemisorption energies [3]. Preliminary calculations indicate, however, that other dissociation sites give much lower barriers in the case of copper and for these pathways the latter explanation is more likely to be relevant.

While the principal features for the dissociation reaction of hydrogen on a nickel surface are fairly well described using only one metal atom, this is not the case for copper. The reason for this behaviour is that while the *d* orbitals, which are quite local in character, largely determine the reaction in the on-top dissociation for nickel, the active metal orbitals are delocalized cluster type orbitals in the copper case. It was found that the reaction can in fact be qualitatively described by a negatively charged triatomic system in this case. All four bonding electrons have to be available in the model triatomic system. This is the case for NiH_2 but only three bonding electrons are available for CuH_2.

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