



# Theoretical study of chemi- and physisorption processes of H<sub>2</sub> molecules on a (100) surface of silver

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## ABSTRACT

A model system consisting of a cluster of 13 Ag atoms and  $n$  ( $n = 1, 2, 3$ ) H<sub>2</sub> molecules has been used to study, by ab initio methods, the structural and energetic characteristics of the chemi- and physisorption processes of H<sub>2</sub> on a (100) surface of silver. The dissociative chemisorption of a first H<sub>2</sub> molecule is analyzed in terms of hydrides formation and it is shown that several electronic states are interacting in the vicinity of the activation barrier leading to complex electronic processes. The energy of the physisorption interaction of the first H<sub>2</sub> molecule for different orientations and that of further H<sub>2</sub> molecules coming directly on top of the first chemisorbed one are determined with highly correlated wavefunctions. As for the (H<sub>2</sub>) <sub>$n$</sub> Cu<sub>13</sub> system, already studied with similar approaches, it is found for the (H<sub>2</sub>) <sub>$n$</sub> Ag<sub>13</sub> system that the physisorption energy of the second layer is enhanced by a factor close to two compared to that of the first layer due to dipolar interactions with the polarized surface. The physisorption energy of the third and further layers tends to the van der Waals H<sub>2</sub>/H<sub>2</sub> interaction energy.

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## 1. Introduction

The H<sub>2</sub>/Cu(100) system has been widely used in surface science as a benchmark for the understanding of molecule-surface interactions, particularly in the domain of catalysis and many theoretical and experimental studies are dealing with the H<sub>2</sub>/Cu dissociative adsorption. No such extensive work has been achieved on the H<sub>2</sub>/Ag system, however several experiments have been reported on physisorbed H<sub>2</sub> on silver surfaces: high resolution electron energy loss spectroscopy (HREELS) of physisorbed H<sub>2</sub> on cold surfaces of Ag has revealed rotational transitions ( $J = 0-2$ ) of para-H<sub>2</sub> at 44 meV and a vibrational transition within the H<sub>2</sub> molecule at 514 meV with no evidence for a H–H bond expansion, but indicating a rather fast para-ortho hydrogen spin transition of the physisorbed molecules [1,2]. Rotational excitation of physisorbed H<sub>2</sub> by low energy electron scattering showed that H<sub>2</sub> molecules parallel to the surface can rotate and move rather freely as rotors on the surface [3]. Several bound states of the van der Waals physisorbed H<sub>2</sub> molecules could also be detected on cold surfaces (10 K and 80 K) by Andersson et al. [4] by rotationally resolved inelastic scattering of H<sub>2</sub> [5] and calculated with a model interaction potential [6] and later by desorption of H<sub>2</sub> from an Ag(111) surface [7].

A theoretical study of H<sub>2</sub>/Ag(100) has been reported by Eichler et al. [8] providing potential energy surfaces (PES) for the interac-

tion of H<sub>2</sub> molecules with a close lying surface of silver atoms for different orientations and relative positions of the H<sub>2</sub> molecules, including the determination of sticking probabilities [9]. These calculations have been performed with the density functional theory (DFT) method, using the VASP program which allows a periodic description of the surface and of a monolayer of hydrogens. The Ag(100) surface is found to be an example where only activated adsorption processes are possible and where the dissociative adsorption is an endothermic process. Activated paths also occurred for the chemisorption of H<sub>2</sub> on Cu(100) surfaces but the adsorption processes are exothermic with this metal, except in the case of tilted orientations and dissociation on top sites [10]. On Pd(100) or Rh(100) surfaces, adsorption is generally non activated [8] except along some specific reaction channels. In a recent paper we have reported the energetic properties of successive layers of H<sub>2</sub> on a copper surface [11] and the main result was that the physisorption energy of a second layer of H<sub>2</sub> on a copper surface already covered by dissociated H<sub>2</sub> molecules is almost twice that of the first H<sub>2</sub> molecule and that this energy strongly depends on the orientation of the molecule with respect to the underlying surface. The bond length of the H<sub>2</sub> molecule in the second layer remains at its standard equilibrium value. Moreover the strong polarization induced by the chemisorbed H atoms on the surface is responsible for the enhancement of the second layer's physisorption energy. The investigation of third layer interactions has shown a significant decrease of the interaction energy compared to that of the second layer, attributed to a screening effect of the non dissociated H<sub>2</sub> molecules in the second layer.

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The purpose of the present work is to study the interactions in the  $\text{H}_2/\text{Ag}(100)$  system and to compare them with those in the copper system [11]. For that purpose we have used a cluster representation of the surface and investigated the electronic structure of the chemisorbed  $\text{H}_2$  molecule and the physisorption energies of the successive layers of  $\text{H}_2$  molecules, including the effect of the relative orientation of the  $\text{H}_2$  molecules.

## 2. Characteristics of the calculation

### 2.1. Description of the model

When a cluster model is used to describe a surface, it is well known that the size of the cluster strongly influences the quality of the results, as it has been shown, for example, in the case of  $\text{Ar}/\text{Ag}(111)$  [12], where the repulsion energy between the metals and the Ar atom is underestimated when small  $\text{Ag}_4$  clusters are used. Studies using larger clusters, like  $\text{Ag}_{10}$ , have given a satisfactory agreement with the slab calculations. Comparable investigations of the interaction of  $\text{H}_2$  with clusters of nickel by Siegbahn et al. [13] proved that interaction energies and geometric parameters of good quality are accessible with clusters containing 13–14 atoms. Consequently, we have chosen for the present study a two layers' cluster, consisting of 13 atoms, which could be written (9, 4), where the two numbers indicate the number of silver atoms in the first and second layer respectively; the atoms are organized to represent a (100) face of the *fcc* crystal of silver. The model is similar to the one used in the previous study on  $\text{H}_2/\text{Cu}(100)$  and details can be found in reference [11]. The interaction energy between the  $\text{H}_2$  molecule and the surface is determined as a function of two parameters ( $Z$ , distance of the center of mass of  $\text{H}_2$  to the center of the central Ag atom in the first layer and  $r$ , the H–H bond length) for selected values of the orientational angles ( $\theta$ ,  $\Phi$ ), as described in Fig. 1. The displacement of the center of mass of the  $\text{H}_2$  molecule is constrained to the  $z$ -axis, perpendicular to the surface.

We have obtained a 2D potential energy surface (PES) within the following approximations: the positions of the silver atoms have been fixed at their experimental positions in the *fcc* lattice and there is no relaxation of the geometry of the silver cluster when the  $\text{H}_2$  molecule approaches. The parameters of the  $\text{Ag}_{13}$  cluster have been taken from Eichler et al. [8] with the Ag–Ag distances fixed at 2.95 Å (5.57 bohr) as it is in the Ag *fcc* crystal. Moreover, we have assumed that the Born-Oppenheimer approximation holds and that the process takes place in the electronic ground state. The reference energy is taken as the energy of the system  $\text{H}_2$  plus cluster separated by 15 Å or  $\text{H}_2$  plus covered clusters separated by 15 Å for the second and third layers.

### 2.2. Computational details

All the calculations have been performed using, for the silver atoms, the effective core pseudopotentials (ECP) developed by Hay and Wadt [14]. Two different ECPs are used to describe the core electrons of the silver atoms: for the central silver atom of the topmost layer, which experiences the largest part of the interaction with  $\text{H}_2$ , a small core ECP (S.ECP) has been used [15], with 19 explicit electrons ( $4s^2 4p^6 4d^{10} 5s^1$ ) in the electronic calculations. For the twelve other Ag atoms, including the two nearest neighbours of the  $\text{H}_2$  molecule on the surface, we have used a large core ECP (L.ECP) [16] such that only the 5s electron of each Ag atom is explicit in the electronic calculations. This ansatz results in a total set of 33 valence electrons. Selected parts of the Gaussian basis set optimized for these pseudopotentials [15,17] which corresponds to a (8s7p6d2f1g) basis contracted into [6s5p3d2f1g], have been used to describe the valence electrons of both types of

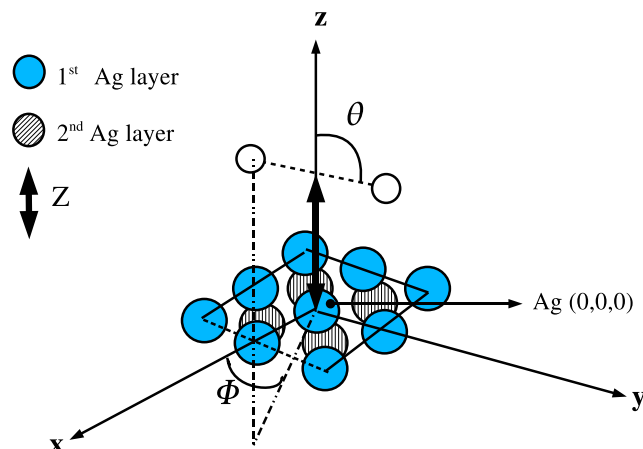


Fig. 1. Description of the coordinates used to study the interaction of  $\text{H}_2$  with the surface of the cluster.

Ag atoms. The basis set for the hydrogen atoms consists in the triple-zeta quality basis sets of Dunning [18] (cc-p-VTZ basis or aug-cc-p-VTZ basis which includes additional diffuse functions). Since highly correlated wavefunctions are necessary for a reliable investigation of such van der Waals interactions, multi-reference-configuration-interaction (MRCI) calculations, with selected reference spaces deduced from a multi-configuration-self-consistent-field (MCSCF) calculation, have been used to determine the electronic structure of the  $(\text{H}_2)_n\text{Ag}_{13}$  systems. We used the  $C_{2v}$  symmetry point group for all the calculations which were performed using the code MOLPRO [19].

### 2.3. Nature of the electronic ground state of $\text{H}_2\text{Ag}_{13}$

When the  $\text{H}_2$  molecule and the  $\text{Ag}_{13}$  cluster are separated, the  $\text{H}_2$  molecule is in the  $X^1\Sigma_g^+$  electronic ground state and the cluster is in a  $^2A_1$  ground state. For large separation, with the  $\text{H}_2$  molecule oriented parallel to the surface, as described in Fig. 1, the overall system can be described in the  $C_{2v}$  symmetry and its electronic ground state is  $^2A_1$ . When the  $\text{H}_2$  molecule is chemisorbed on the surface, there is an electron transfer from the metals toward the hydrogens leading to the formation of hydrides. This electron transfer induces a modification of the electronic wavefunction which can be compared with the situation occurring in the  $\text{H}_2\text{Ag}$  system. In a recent investigation of the dihydrides of group I–B metals, ( $M = \text{Cu}, \text{Ag}, \text{and Au}$ ), Guitou and Chambaud [20] showed that the  $\text{MH}_2$  radicals have a metastable  $^2B_2$  bent ground state separated from the dissociation into  $[M + \text{H}_2]$   $^2A_1$  ground state by barriers evaluated to 1.43, 0.78 and 0.80 eV, for Cu, Ag and Au compounds, respectively. The modification of the electronic wavefunction during the formation of  $\text{MH}_2$  from  $M + \text{H}_2$  is explained by the transfer of electrons from the metal to the antibonding  $\sigma_u$  orbital of  $\text{H}_2$  (of  $b_2$  symmetry in the supersystem  $\text{MH}_2$ ) leading to the formation of hydrides. Since a similar charge transfer occurs during the chemisorption of  $\text{H}_2$  on the metallic surface [11], one can expect comparable features, namely the presence of an activation barrier in the entrance channel, an endothermic adsorption (similar to the formation of a metastable state for  $\text{MH}_2$ ) and a modification of the nature of the electronic ground state.

As in the molecular process, an activation barrier has been detected experimentally for the chemisorption of  $\text{H}_2$  on copper and silver surfaces. Moreover the chemisorption process is found experimentally endothermic for  $\text{H}_2$  on silver, but exothermic for  $\text{H}_2$  on copper: by comparison  $\text{H}_2\text{Ag}$  ( $X^2B_2$  state) was found endothermic by 1.60 eV with respect to  $[\text{Ag}(^2S) + \text{H}_2(^1\Sigma_g^+)]$ , when

$\text{H}_2\text{Cu}(\text{X}^2\text{B}_2 \text{ state})$  was endothermic by only 0.45 eV [20]. These results indicate that the main effects are comparable in both molecular and surface processes, but the surface process is more complex because of possible delocalization and the chemisorbed systems are more stabilized than the associated molecular ones.

Since the  $\text{C}_{2v}$  symmetry is preserved when the  $\text{H}_2$  molecule approaches parallel to the surface along the  $z$ -axis, the situation is comparable to that of a bent  $\text{MH}_2$  system and we have to check the symmetry of the electronic ground state along the chemisorption process. In the case of  $\text{H}_2\text{Cu}_{13}$ , the MRCI calculations with different basis sets give always the  $^2\text{A}_1$  for the ground state, however additional DFT calculations [21] have shown a contamination of this  $^2\text{A}_1$  due to a close lying  $^2\text{B}_2$  state at short distances. We have thus investigated the symmetry of the ground state of  $\text{H}_2\text{Ag}_{13}$  and the corresponding discussion is presented in the next section.

### 3. Results and discussion

#### 3.1. $\text{H}_2\text{Ag}_{13}$ system

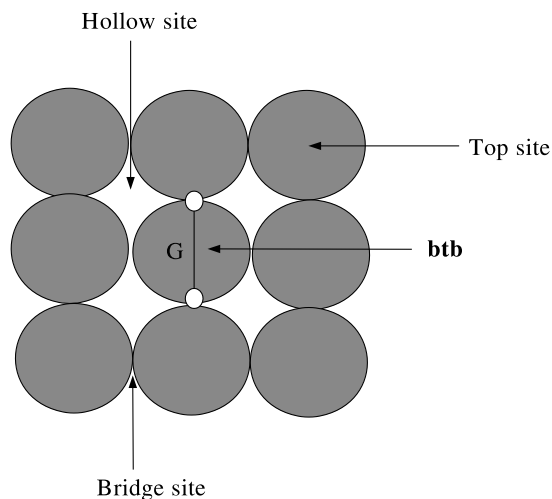
The calculations of the electronic energy of the  $\text{H}_2\text{Ag}_{13}$  system include a MCSCF step followed by a MRCI calculation. In the MCSCF step, 7 orbitals of the central Ag atom have been frozen and the corresponding 14 electrons have not been correlated. The electronic configurations involved in the MCSCF calculations are thus obtained by allowing the excitations of the 19 other valence electrons into 14 active orbitals, leading to 229244 configuration state functions (CSFs). A selection of about 6000 configurations, with a weight larger than 0.0005 in the expansion of the MCSCF wavefunction, is then used as reference space for the subsequent MRCI calculations. The interaction energy has been studied as a function of the two parameters defined in Section 2,  $Z$  and the internuclear distance  $\text{H}-\text{H}$  ( $r$ ): the angle  $\theta$  of the hydrogen molecule axis with the  $z$ -axis was set to  $90^\circ$  ( $\text{H}_2$  molecular axis parallel to the cluster) and  $\phi$  was set to  $0^\circ$  for a path corresponding to a *btb* (bridge-top-bridge) situation, described in Fig. 2. Upright  $\text{H}_2$  was also studied, corresponding to  $\theta = 180^\circ$ . Our results are compared with those of Eichler et al. [8], who studied the dissociative chemisorption of  $\text{H}_2$  on a  $\text{Ag}(100)$  surface using the density functional theory (DFT) approach. According to recent calculations by Kokh et al. [22] employing the embedded cluster model and highly correlated wavefunctions, even though hollow sites are energetically favored for most of the molecular chemisorbed species, the difference in

the binding energies between hollow, top and bridge sites is rather small if the bond has a large fraction of ionic character, which is the case in the present situation. Such results confirmed the DFT calculations of Eichler et al. [8] who found an energy difference smaller than 0.1 eV between the binding energies in hollow or bridge sites. Since the different sites of chemisorption possess roughly the same energy and correspond to stable or metastable minima, we have chosen to work here with the *btb* orientation of the  $\text{H}_2$  molecule because it allows additional symmetry simplifications within our cluster model.

##### 3.1.1. $\text{H}_2$ parallel to the cluster in a *btb* position

For each value of the distance  $Z$  of the  $\text{H}_2$  molecule from the surface, the  $\text{H}-\text{H}$  internuclear distance ( $r$ ) has been optimized in order to get the minimum energy path. At large separations, this optimized internuclear distance is equal to the equilibrium distance in the free  $\text{H}_2$  molecule,  $r = 0.74 \text{ \AA}$  (1.4 bohr).

With our model, using a basis set consisting of *spdf* functions on the central Ag atom, *sp* functions on the other Ag atoms and aug-cc-p-VTZ on the H atoms, the physisorption well characterizing the long range interaction between  $\text{H}_2$  and the  $\text{Ag}(100)$  surface has been calculated to be 26.9 meV ( $217 \text{ cm}^{-1}$ ) at the MRCI plus Davidson correction level of theory (MRCI + Q), (see Table 1). The minimum of energy is located at a distance  $Z_{1,P,\text{para}} = 3.90 \text{ \AA}$  (the subscript specifies that it is the position of the physisorption minimum ( $P$ ) of the first  $\text{H}_2$  molecule (1) oriented parallel to the surface (*para*)) and corresponds to a  $\text{H}_2$  molecule at its equilibrium bond length. The experiments on the physisorption of  $\text{H}_2$  on  $\text{Ag}(111)$  and  $\text{Ag}(110)$  surfaces by Andersson et al. [4,23] allowed to assess a physisorption energy of about 32 meV ( $260 \text{ cm}^{-1}$ ) for these systems. In recent experimental analysis of the effect of the anisotropy on the physisorption interaction it has been shown that this energy does not depend on the crystal face in the case of  $\text{H}_2/\text{Cu}$  interactions [24], but strongly does in the case of aluminium surfaces [25,26]. If silver surfaces behave like copper ones, we can estimate the physisorption energy of  $\text{H}_2/\text{Ag}(100)$  to be roughly equal to that of  $\text{H}_2/\text{Ag}(111)$ . Andersson et al. [4] deduced also from their observations a trend of increasing physisorption interaction of  $\text{H}_2$  with noble metals in the series Cu, Ag, and Au. Our results show instead that the physisorption energy for  $\text{H}_2/\text{Ag}(100)$  is slightly smaller than for  $\text{H}_2/\text{Cu}(100)$  which was found equal to 28 meV ( $228 \text{ cm}^{-1}$ ) [11]. In the present case it was necessary to include at least *p* functions on the twelve external Ag atoms in order to get a converged physisorption energy; with only *s* functions on these atoms, the calculated physisorption energy was only 12 meV ( $96.8 \text{ cm}^{-1}$ ) instead of 26.9 meV. Calculations with additional *g* functions on the central Ag atom give a slightly larger interaction energy of 27.3 meV, quite comparable to that of the Cu system. The basis set superposition error (BSSE) correction has not been



**Fig. 2.** The three possible sites, hollow(h), top(t) and bridge(b) of the H atoms on the (100) surface of Ag (grey disks). On this figure one  $\text{H}_2$  molecule (white disks) is in a (*btb*) situation.

**Table 1**

Physisorption energies,  $E_{n,P}$  in meV (in  $\text{cm}^{-1}$  in the parenthesis) at the equilibrium geometries,  $Z_{n,P}$  in  $\text{\AA}$  for two investigated orientations of  $\text{H}_2$  approaching  $\text{Ag}_{13}$  ( $E_{1,P}$  and  $Z_{1,P}$ ) and  $\text{Ag}_{13}\text{H}_2$  ( $E_{2,P}$  and  $Z_{1,P}$ )

	$\text{H}_2 \parallel \text{Ag}_{13}$	$\text{H}_2 \perp \text{Ag}_{13}$	$\text{H}_2 \parallel \text{H}_2\text{Ag}_{13}$	$\text{H}_2 \perp \text{H}_2\text{Ag}_{13}$
$E_{1,P}$ MRCI	14.5 (117)	28.0 (226)	–	–
$Z_{1,P}$	4.10	4.18	–	–
$E_{1,P}$ MRCI + Q	26.9 (217)	37.0 (298)	–	–
Ref. [23]	32			
$Z_{1,P}$	3.90	3.95	–	–
$E_{2,P}$ MRCI	–	–	26.3 (212)	56.7 (457)
$Z_{2,P}$	–	–	3.97	3.96
$E_{2,P}$ MRCI + Q	–	–	35.9 (289)	66.9 (539)
$Z_{2,P}$	–	–	3.90	3.87

The equilibrium bond length of the  $\text{H}_2$  approaching the surface is equal to the equilibrium geometry of an isolated  $\text{H}_2$ ,  $r_e = 0.74 \text{ \AA}$ .

incorporated in the present treatment because it is rather small (estimated to  $3 \text{ cm}^{-1}$  close to the minimum of physisorption) and we cannot expect to reach such an accuracy in our calculations on the interaction energies because of the approximations introduced in our model. Our expected accuracy is rather in the range of  $10 \text{ cm}^{-1}$ .

Closer to the surface, the  $\text{H}_2$  bond length remains constant as long as  $Z$  is larger than  $1.30 \text{ \AA}$  ( $2.46 \text{ bohr}$ ), then the  $\text{H}_2$  molecule starts to stretch until the equilibrium distance, corresponding to H adsorbed on the surface, is reached.

Using a basis set consisting of *spdf* functions on the central Ag atom, *sp* functions on the other Ag and aug-cc-p-VTZ on the H atoms, the minimum of the chemisorption energy for  $\text{H}_2\text{Ag}_{13}$ , corresponding to an endothermic process of  $0.60 \text{ eV}$ , is found for  $Z_{1,c} = 1.07 \text{ \AA}$  ( $2.02 \text{ bohr}$ ) and  $r = 2.89 \text{ \AA}$  ( $5.46 \text{ bohr}$ ),  $0.06 \text{ \AA}$  smaller than the lattice parameter of the Ag fcc crystal corresponding to the bridge-bridge distance. The difference in  $r$  is probably due to the different representation used for the metal atoms, it is however within the accuracy required to describe the next step of the present study and it does not affect the description of the charge transfer between the H and the Ag atoms. The chemisorption energy is in quite good agreement with that obtained by Eichler et al. [8] with a periodic description of the chemisorbed molecules. The difference of  $0.19 \text{ eV}$  can be partly attributed to the restrictions introduced in the description of the metallic atoms other than the central one and partly to the fact that our model cannot take into account the interactions between the  $\text{H}_2$  molecules on the surface. This later effect depends on the rate of coverage of the surface and for a similar situation in the case of the  $\text{H}_2\text{Cu}_{13}$  system it was estimated to introduce an error of  $0.1 \text{ eV}$ . In Fig. 3 we have reported the energy curve of Eichler et al. [8] for the *btb* chemisorption path and our calculated energy profile of the  $^2A_1$  state at short range interaction of  $\text{H}_2$  with the model Ag(100) surface. The agreement is satisfactory for the short and long range interactions, but not for the barrier.

As already mentioned for the  $\text{H}_2\text{Cu}_{13}$  system [11], the height of the dissociation or activation barrier is overestimated in our calculations compared to slab calculations and there are several reasons for that. One of the reasons can be a strong modification of the electronic wavefunction in the vicinity of the barrier. To explicit

this point we have calculated the energy profiles of the minimum energy path in the four possible symmetries compatible with our system, namely  $A_1$ ,  $B_2$ ,  $B_1$  and  $A_2$ . It has been found that the two lowest doublet states are in  $^2A_1$  and  $^2B_2$  symmetries. The potential curves of these two states are reported in Fig. 4, the corresponding data are given in Table 2. As for the  $\text{AgH}_2$  system [20], the  $^2A_1$  state is the lowest one at large intersystem distance, then it crosses the  $^2B_2$  state when  $Z$  decreases, but contrary to the  $\text{AgH}_2$  system, the ground state in the chemisorption region is again the  $^2A_1$  state. This difference between the  $\text{AgH}_2$  molecule and the  $\text{H}_2\text{Ag}_{13}$  cluster can be explained by the direct participation of the two neighbouring Ag atoms in the bonding  $a_1$  orbital, which stabilizes the  $^2A_1$  state by spreading the positive charge on more than one metallic atom. In the region of the crossings there are conical intersections between the two electronic states: we have interpolated a minimum energy curve which follows the lowest state for all the geometries. This interpolated curve gives an idea of a possible minimum energy path on the potential energy surface. In our cluster calculations we are always following a state of a given symmetry, which is not the case in DFT calculations nor in experiments where the state with the lowest energy is always accessible. This can explain why calculated barriers, obtained with symmetry constraints, are higher than the experimental one, and the interpolated barrier drawn in Fig. 4 and evaluated to be close to  $1.8 \text{ eV}$  is certainly a better representation of the actual barrier.

In order to quantify the charge transfer occurring when the  $\text{H}_2$  molecule is chemisorbed on the surface we have calculated the dipole moment of the  $\text{H}_2\text{Ag}_{13}$  system at its equilibrium geometry. As a result of the electron transfer,  $\text{H}^{\delta-}$  and  $\text{Ag}^{\delta+}$  species are formed leading to a dipole moment along the  $z$ -axis (for symmetry reason, it is the only non zero component of this dipole moment) which has been calculated  $\mu = 0.55 \text{ Debye}$  (MRCI level). Because we are using a cluster model to represent the surface it is necessary to compare this quantity with the value of the dipole moment of the cluster alone which is not strictly zero but calculated  $-0.21 \text{ Debye}$  (MRCI level) as an artefact due to the limited size of the cluster and the different treatment of the Ag atoms. We thus observe an increase of  $0.76 \text{ Debye}$  of the dipole moment perpendicular to the surface related to the chemisorption process.

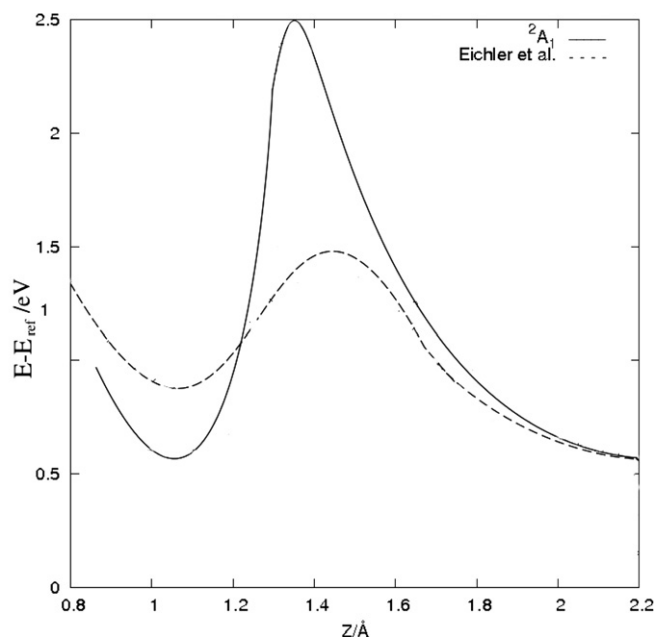


Fig. 3. Interaction energy in the  $\text{H}_2/\text{Ag}(100)$  system calculated by Eichler et al. [8] (dash line) and this work (full line) for a (*btb*) pathway.

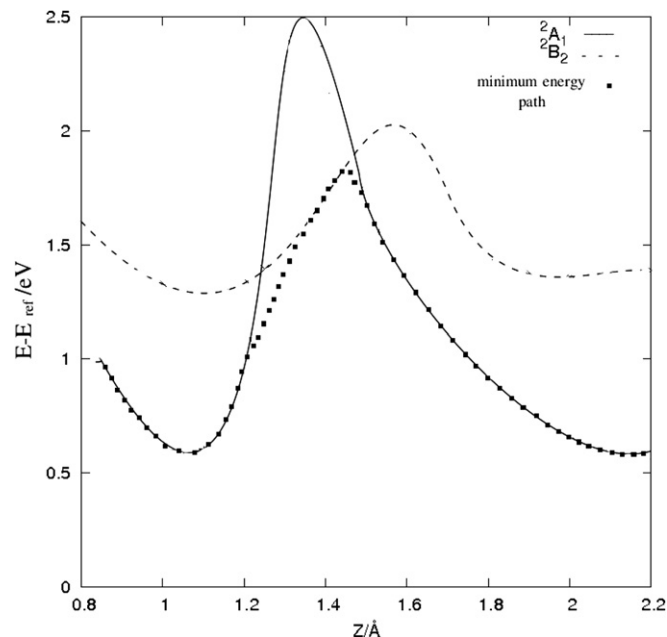


Fig. 4. Minimum energy paths close to the barrier in  $^2A_1$  and  $^2B_2$  symmetries. The interpolated curve shows a possible global minimum energy path.



**Table 2**Data calculated for  $\text{H}_2/\text{Ag}_{13}$  at the barrier and for the chemisorption equilibrium

Processes	Energy/eV		$Z/\text{\AA}$		$r/\text{\AA}$	
Activation barrier	2.61 <sup>a</sup>	1.44 <sup>b</sup>	1.3 <sup>a</sup>	1.45 <sup>b</sup>	1.6 <sup>a</sup>	1.66 <sup>b</sup>
	1.8 <sup>A</sup>	–	1.47 <sup>A</sup>	–	–	–
Chemisorption	0.6 <sup>a</sup>	0.79 <sup>b</sup>	1.07 <sup>a</sup>	1.03 <sup>b</sup>	2.89 <sup>a</sup>	2.94 <sup>b</sup>

The reference energy is the energy of  $\text{H}_2$  plus  $\text{Ag}_{13}$  separated by 15  $\text{\AA}$ .<sup>A</sup> These values correspond to the barrier obtained by interpolation of the minimum energy path deduced from the crossing between the  $^2\text{A}_1$  and the  $^2\text{B}_2$  states.<sup>a</sup> This work.<sup>b</sup> Ref. [8].

### 3.1.2. $\text{H}_2$ perpendicular to the cluster on top of the central Ag

When the  $\text{H}_2$  molecule approaches perpendicularly the surface, we found a physisorption well of 37.0 meV ( $298\text{ cm}^{-1}$ ) (MRCI + Q level), located at  $Z_{1,P,\text{perp}} = 3.95\text{ \AA}$  (7.5 bohr), the subscript (perp) refers here to the perpendicular orientation of the  $\text{H}_2$  molecule. The central Ag atom, represented by a small core pseudopotential (S.ECP), perceives the major effect of this interaction. Contrary to the conclusions deduced from the low energy electron scattering experiments [3] the physisorption interaction is found anisotropic, as expected from the anisotropy of the polarizability of the  $\text{H}_2$  molecule. If one can easily foresee that the rotational motion of the physisorbed  $\text{H}_2$  molecule in a plane parallel to the surface is only slightly perturbed by the physisorption interaction, it should not be the case for a rotational motion in a plane perpendicular to the surface because of the anisotropy of the interaction. Since the rotation is coupled with the stretching along the van der Waals coordinate  $Z$ , and since the rotational energy of  $\text{H}_2$  molecules is of the same order of magnitude as the physisorption energy, it is highly probable that such a rotational motion should rapidly lead to the dissociation of the physisorbed complex.

There is no chemisorption for this orientation of the  $\text{H}_2$  molecule, in agreement with other studies on upright  $\text{H}_2$  on copper surfaces [27,11], on silver and on other metallic surfaces [8].

As expected from the anisotropy of the  $\text{H}_2$  molecule, the  $E_{1,P,\text{perp}}$  is found larger than  $E_{1,P,\text{para}}$ : at the MRCI level a ratio of 1.93 is calculated between both energies, this ratio reduces to 1.37 at the MRCI + Q level where a larger part of the correlation energy is introduced. These interactions mainly result from the dispersion interaction and the calculated ratio is in very good agreement with the expected ratio which should be close to 1.30 according to the values of the polarizability of the  $\text{H}_2$  molecule along its nuclear axis,  $\alpha_{\parallel} = 0.932\text{ \AA}^3$  [28] and perpendicular to it,  $\alpha_{\perp} = 0.716\text{ \AA}^3$ .

## 3.2. $(\text{H}_2)_2\text{Ag}_{13}$ system: second layer effect

### 3.2.1. Description of the system

The  $\text{H}_2\text{Ag}_{13}$  system, in a *btb* chemisorption situation, has been fixed at the equilibrium geometry determined in the previous section; the internuclear distance in the dissociated  $\text{H}_2$  molecule is fixed at 2.89  $\text{\AA}$  and the center of mass of  $\text{H}_2$  is localized at  $Z_{1,C} = 1.07\text{ \AA}$ . A second  $\text{H}_2$  molecule is moved towards the surface and the energy of this  $(\text{H}_2)_2\text{Ag}_{13}$  system is calculated as a function of  $Z$ , distance from the center of mass of this second molecule to the center of the central Ag atom, and of the H–H bond length of this second molecule, for two orientations of this molecule (parallel to the first one and to the surface and perpendicular to the surface on top of the central Ag atom). Since the global symmetry of the supermolecule can be described with the  $\text{C}_{2v}$  symmetry, and since the second  $\text{H}_2$  molecule is in its  $X^1\Sigma_g^+$  electronic ground state, the symmetry of the electronic ground state of the supersystem  $(\text{H}_2)_2\text{Ag}_{13}$  is that of the chemisorbed  $\text{H}_2\text{Ag}_{13}$  system, as explicated in the previous section. We have thus performed calculations of the  $^2\text{A}_1$  state involving, in the MCSCF step, 21 active electrons

and a set of 14 active orbitals, leading to 46222 CSFs for the parallel or perpendicular approach of the incoming  $\text{H}_2$ . The set of active orbitals for the MCSCF calculations has been designed in such a way that the  $\sigma_u$  orbital of the second  $\text{H}_2$  molecule is included for both orientations. Subsequent MRCI calculations have been performed using all the configurations generated in the MCSCF step as reference space.

### 3.2.2. Results

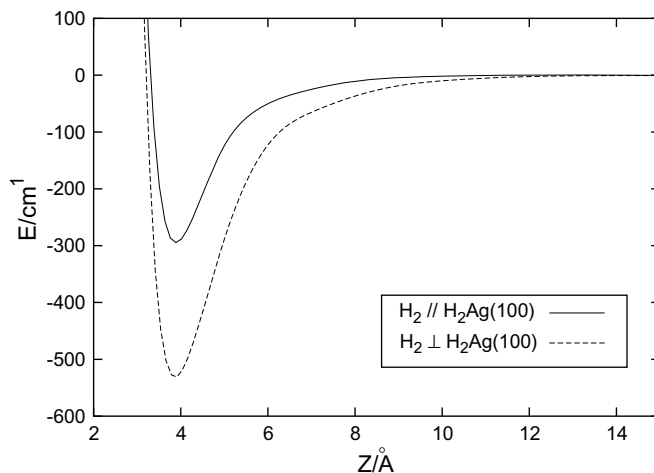
The optimization of the bond length ( $r$ ) of the second  $\text{H}_2$  for each  $Z$  value along the reaction path showed that  $r$  remains, for all  $Z$ , at the equilibrium value of the isolated molecule,  $r_e = 0.74\text{ \AA}$  (1.4 bohr), or very close to it even at the minimum of the physisorption well and for both relative orientations of the two  $\text{H}_2$  species. This result shows that the  $\text{H}_2$  molecule in this second layer is stabilized energetically in this position but only slightly modified by the underlying metallic surface. Its polarization is such that the electronic cloud is slightly pushed away from the surface. The same effect was observed for the first physisorbed layer but to a lesser extent. The potential energy functions  $V_2(Z)$  representing the interaction energy of  $\text{H}_2$  with  $\text{H}_2\text{Ag}_{13}$ , calculated at the MRCI + Q level, is presented in Fig. 5 and the structural parameters are given in Table 1.

As for the first layer, we found a slightly stronger interaction of the  $\text{H}_2$  molecule with the copper surface [11] than with that of silver, however several features of the interactions of  $\text{H}_2$  with the Ag(100) surface are found similar to those with the Cu(100) surface:

- The interaction energies of the second layer are larger than those of the first layer:

$$E_{2,P,\text{perp}} > E_{1,P,\text{perp}} \quad \text{and} \quad E_{2,P,\text{para}} > E_{1,P,\text{para}}$$

- $E_{2,P,\text{perp}}$  is larger than  $E_{2,P,\text{para}}$ , at the MRCI level a ratio of 2.15 is found between both energies, this ratio reduces to 1.85 at the MRCI + Q level. This effect partly results from the dipole/induced dipole interaction and from the dispersion interaction which would lead to a ratio close to 1.30 as obtained for the first layer. In the second layer, there are additional steric effects playing a role. For these second layer's  $\text{H}_2$  molecules, the closest atoms are the negatively charged, highly polarizable hydrogen atoms chemisorbed on the surface and the largest effects are obtained when the two systems can approach each other closely. This is



**Fig. 5.** Calculated second layer physisorption energy (MRCI + Q) of  $\text{H}_2/\text{H}_2\text{Ag}_{13}$  and  $\text{H}_2 \perp (\text{H} + \text{H} + \text{Ag}_{13})$  as a function of the distance  $Z$  to the surface.

the case for the perpendicular geometry where the second layer's  $H_2$  molecule can come closer to these negatively charged hydrogens; the distances between one coming H and the closest chemisorbed H is 2.84 Å in the perpendicular approach and 3.03 Å in the parallel one – the distances of the same H to the central Ag atom is 3.50 Å and 3.91 Å, respectively. This steric effect explains why the perpendicular second layer's  $H_2$  molecule is significantly more stable than the parallel one. Such a result is reliable with our model since the main effects involved in this process are related to the chemisorbed structure which has been shown to be appropriately described by such clusters.

### 3.3. $(H_2)_n Ag_{13}$ system: third and further layer interactions

The  $H_2$  molecules in the third layer are localized far from the surface, at approximately 7 Å (13 bohr). Considering the shape of the curve describing the interaction energy  $V_2(Z)$  presented in Fig. 5, one can see that, at these large distances, the interactions are of the same order of magnitude as the  $H_2/H_2$  interaction energy. In order to determine the interaction energy  $V_3(Z)$  of one  $H_2$  molecule with the metallic surface covered by two layers of  $H_2$  molecules, we have used a simple model based on the additivity of two contributions, the interaction of one  $H_2$  molecule with the metallic surface covered by one dissociated  $H_2$  molecule, and the interaction of one  $H_2$  molecule with another  $H_2$  molecule:

- $V_2(Z)$ , calculated in the previous section, at the MRCI + Q level, represents the interaction energy of one  $H_2$  molecule with the metallic surface covered by one dissociated  $H_2$  molecule. We are exploring the long range part of this potential and we assume that the small modification along the  $z$ -axis due to the presence of the second molecule does not induce a large perturbation of this potential.
- $V_{H_2/H_2}$  is the van der Waals interaction between two  $H_2$  molecules. Tests calculations of this interaction with our ansatz to describe the  $H_2$  molecules proved that only 75% of this energy can be recovered [11]. Consequently, we preferred to use here the potentials of Boothroyd et al. [29], which are the most accurate potentials on the supermolecule  $H_4$  available so far.

$$V_3(Z) = V_2(Z) + V_{H_2/H_2}(Z - Z_{2,p})$$

where  $Z_{2,p}$  is the position of the  $H_2$  molecule in the second layer (minimum of the physisorption well for the corresponding orientation of the second  $H_2$  molecule). The potential curves  $V_3(Z)$ , for different orientations of the third  $H_2$  molecule are plotted in Fig. 6. The interaction energies  $E_{3,p}$  and the positions  $Z_{3,p}$  at the minimum of these curves are summarized in Table 3. In this Table, a notation such as  $H_2 \parallel (H_2 \perp Ag_{13}H_2)$  means that the third molecule is parallel to the underlying system consisting of a second layer's molecule  $H_2$  oriented perpendicularly to the chemisorbed surface  $Ag_{13}H_2$ .

Since  $Z_{2,p}$  is almost the same for the two different orientations of the second  $H_2$  molecule, the equilibrium position  $Z_{3,p}$  of the third  $H_2$  molecule depends on two factors: the relative orientation of the  $H_2$  molecule in the third layer compared to that of the second layer, and the strength of  $V_2(Z)$  for distances close to 7 Å. Considering the first factor, it is clear that  $H_2$  molecules can come closer when they are perpendicular (case  $\parallel/\perp$  and  $\perp/\parallel$ ) than when they are parallel (case  $\parallel/\parallel$ ) or even less when they are aligned (case  $\perp/\perp$ ). Due to the addition of the two attractive interactions, the equilibrium distances between the  $H_2$  molecules of the second and third layer ( $Z_{3,p} - Z_{2,p}$ ) are smaller than between two free  $H_2$  molecules with similar orientations. These data can be compared to the  $H_2/H_2$  van der Waals interactions from Boothroyd et al. [29] in corresponding orientations. The third layer interaction energies are

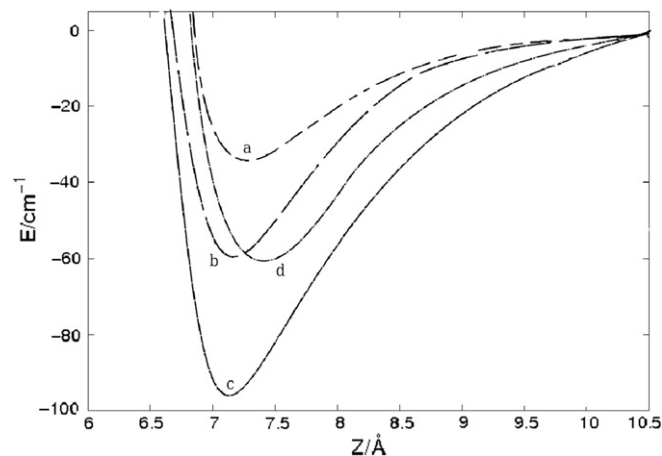


Fig. 6. Calculated third layer physisorption energy of  $H_2$  with the silver surface covered by hydrogens, as a function of the distance  $Z$  to the surface. The curves refer to the following situations: (a)  $H_2 \parallel (H_2 \parallel Ag_{13}H_2)$ , (b)  $H_2 \parallel (H_2 \perp Ag_{13}H_2)$ , (c)  $H_2 \perp (H_2 \parallel Ag_{13}H_2)$ , (d)  $H_2 \perp (H_2 \perp Ag_{13}H_2)$ .

Table 3

Third layer interaction energies for four relative orientations:  $\parallel$  and  $\perp$  refer to the orientation of the molecule with respect to the surface

$H_2$ on $Ag(100)$ surface	$E_{3,p}$ MRCI + Q	$Z_{3,p}$	$Z_{3,p} - Z_{2,p}$
$H_2 \parallel (H_2 \parallel Ag_{13}H_2)$	34.62	7.26	3.36
$H_2 \parallel (H_2 \perp Ag_{13}H_2)$	59.39	7.15	3.25
$H_2 \perp (H_2 \parallel Ag_{13}H_2)$	95.68	7.10	3.23
$H_2 \perp (H_2 \perp Ag_{13}H_2)$	61.10	7.37	3.50
$H_2/H_2$	$E_{BMKP}$ [29]		$Z_e$
$H_2 \parallel H_2$	16.9		3.45
$H_2 \perp H_2$	41.3		3.26
$H_2 - H_2$	13.0		3.75

$E_{3,p}$  are given in  $cm^{-1}$  and  $Z_{3,p}$  in Å. For  $H_2/H_2$  the values are the interaction energies ( $E_{BMKP}$ ) at the minimum ( $Z_e$ ) of the corresponding potentials.

small compared with those of the second layer and already close to the  $H_2/H_2$  interaction energies, as it was obtained with the Cu surface. These results validate our additive approximation.

For the fourth and further layers, the physisorption energy is dominated by the  $H_2/H_2$  interactions since the interaction with the surface  $V_2(Z)$  is only 1  $cm^{-1}$  and 5.6  $cm^{-1}$  for the parallel and

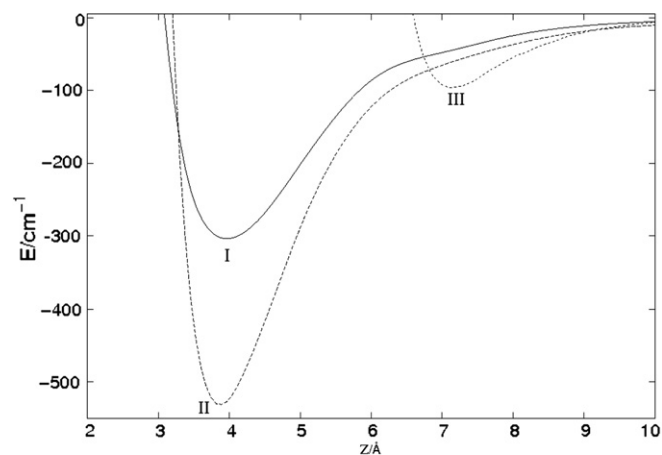


Fig. 7. Physisorption energy of the successive layers of  $H_2$  with the silver cluster as a function of the distance  $Z$  to the surface. (I) corresponds to the perpendicular approach of the first molecule, (II) to the perpendicular approach of the second molecule, and (III) to the parallel approach of the third molecule on a second perpendicular layer.

perpendicular orientation respectively at 10.5 Å close to the distance where the fourth H<sub>2</sub> molecule is to be located.

In order to have an overview of the interaction energies and of the position of the equilibrium minima corresponding to the successive layers we have plotted in Fig. 7 the physisorption energy curves of the first, second and third layer of H<sub>2</sub> molecules interacting with a (100) surface of Ag, for selected orientations of the H<sub>2</sub> molecules.

#### 4. Conclusions

The interaction energies of successive layers of H<sub>2</sub> molecules with a (100) surface of silver have been determined using a cluster consisting of 13 atoms to model the surface. In order to properly describe all these systems, large part of the correlation energy, beyond the MCSCF level of theory, is required. It has been shown that one H<sub>2</sub> molecule approaching a covered surface to form a second layer of molecules lies approximately at 4 Å from the surface and interacts more strongly with the surface than the first incoming molecule: the interaction is almost twice as large but does not lead to a dissociative adsorption because of the presence of the first layer. The perpendicular orientation of this second molecule with respect to the surface is more stable than the parallel one. This interaction is much larger than the van der Waals interaction between two isolated H<sub>2</sub> molecules due to the formation of hydrides on the surface and it stabilizes the molecule in this second layer. The interaction of a third layer, located approximately at 7 Å from the surface, is much smaller than that of the second one and only slightly larger than the van der Waals H<sub>2</sub>/H<sub>2</sub> interaction. By extrapolation, we can say that further layers do not feel anymore the presence of the metallic surface and H<sub>2</sub> molecules behave freely as in the gas phase. Because of the large effect of the second layer, the most favourable coverage of the metallic surface corresponds to a perpendicular orientation of the molecules relative to the

surface for the second layer and then a third layer with molecules oriented parallel to the surface.

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