

## Defect effects on H<sub>2</sub> dissociative adsorption on the Ni(100) surface

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 1219

(<http://iopscience.iop.org/0953-8984/6/6/024>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 14:46

Please note that [terms and conditions apply](#).

## Defect effects on H<sub>2</sub> dissociative adsorption on the Ni(100) surface

Xie Jianjun<sup>†‡</sup>, Jiang Ping<sup>†‡</sup> and Zhang Kaiming<sup>†‡</sup>

<sup>†</sup> CCAST (World Laboratory), PO Box 8730, Beijing 100080, People's Republic of China

<sup>‡</sup> Department of Physics, Fudan University, Shanghai 200433, People's Republic of China

Received 13 July 1993, in final form 17 September 1993

**Abstract.** The dissociative adsorption of a hydrogen molecule on the nickel(100) surface with point defects is investigated using the embedded-atom method (EAM). The potential-energy surfaces (PES) for H<sub>2</sub> dissociation on both perfect and imperfect Ni(100) surfaces are presented, based on total-energy calculations. It is clearly shown that as the H<sub>2</sub> approaches the Ni(100) surface along the entrance channel, the H–H bond is progressively weakened while the H–metal bonds begin to form; finally the H<sub>2</sub> is adsorbed on the surface in the form of two independent H atoms. This dissociation process is affected by the vacancy and impurity atoms existing in the Ni substrate. The activation barriers ( $E_a$ ) for the dissociation of H<sub>2</sub> through various pathways are calculated. The barriers for the dissociation of H<sub>2</sub> on the perfect Ni(100) surface are found to be low (about 0.08–0.09 eV, corresponding to different dissociation pathways). The existence of vacancies enhances the dissociation of H<sub>2</sub> by lowering the activation barrier height and providing more adsorption sites. However, the impurity atoms (Cu, Pd) can impede the dissociation of H<sub>2</sub> on the Ni(100) surface by increasing the activation barrier height. The adsorption heat of H<sub>2</sub> chemisorption on the contaminated Ni(100) surface is also calculated. It is found that the effects of impurities on the dissociation of H<sub>2</sub> vary with the dissociation pathways and the impurity sites.

### 1. Introduction

The dissociative chemisorption of H<sub>2</sub> on a transition-metal surface has been an attractive field due to its importance in catalysis. Many experimental studies [1–3] have been carried out on the H<sub>2</sub>/Ni system using molecular-beam techniques. It is realized that dissociation of H<sub>2</sub> is likely to occur if it is adsorbed on an Ni surface and that the activation barrier height is very low during the adsorption process. For a real surface, some defects, such as impurities and vacancies, always exist. Investigations of the effects of surface defects on the adsorption of H<sub>2</sub> on Ni have been made experimentally by Rendulic *et al* [4]. It is found that the defects and O impurities can generate additional adsorption sites and that these sites are predominantly active at low temperature. Most theoretical approaches [5–9] mainly concentrate on revealing the physical mechanism of H<sub>2</sub> dissociation on the pure Ni substrate. At present there are only a few theoretical investigations on the vacancy and impurity effects on the dissociative adsorption of H<sub>2</sub> on the Ni surface.

Based on the density-functional theory, Daw and Baskes [10] developed a method called the embedded-atom method (EAM) as a new approach for calculating the ground-state properties of a realistic metal system. The EAM has been successfully applied to many fields of metals, impurities, and alloys including bulk, surface, and liquid properties [10–15]. In the present paper, we apply the EAM to the interaction between the H<sub>2</sub> molecule and the

Ni surface and try to investigate the effects of impurities and vacancies on the dissociative adsorption of  $H_2$  on an Ni(100) substrate. The potential for  $H_2$  on the Ni(100) surface is obtained, based on total-energy calculations. Different adsorption sites and dissociation pathways are considered.

## 2. The embedded-atom method and its application to the $H_2/Ni$ system

The basic equations of the EAM are

$$E_{\text{tot}} = \sum_i F_i(\rho_{h,i}) + \frac{1}{2} \sum_j \sum_{i,i \neq j} \Phi_{ij}(R_{ij}) \quad (1)$$

$$\rho_{h,i} = \sum_{j,(j \neq i)} f_j(R_{ij}) \quad (2)$$

where  $E_{\text{tot}}$  is the total energy and  $\rho_{h,i}$  is the electron density at atom  $i$  due to all other atoms.  $f_j$  is the electron density of atom  $j$  at the site of atom  $i$  and  $R_{ij}$  is the distance between atoms  $i$  and  $j$ ;  $F_i(\rho_{h,i})$  is the energy to embed atom  $i$  in an electron density  $\rho_{h,i}$ , and  $\Phi_{ij}$  is a two-body central potential between atoms  $i$  and  $j$ . Equation (2) shows that the host electron density  $\rho_{h,i}$  is assumed to be a linear superposition of contributions from individual atoms, each of which is assumed to be spherically symmetric.

Mei *et al* [15] present a simple analytic form of EAM potentials in FCC metals (such as Cu, Ni, Pd, Au, Ag, Pt) for dynamic simulations, which is valid for any choice of cut-off distance. All atomic potentials beyond the cut-off distance can be neglected. According to Mei *et al*, the total energy for a perfect crystal consisting of  $N$  atoms can be written as

$$E = N \left[ F(\rho) + \frac{1}{2} \sum_m s_m \phi(r_m) \right] \quad (3)$$

$$\rho = \sum_m s_m f(r_m) \quad (4)$$

where  $r_m$  is the distance between a given atom and its  $m$ th neighbours and  $s_m$  is the number of  $m$ th-neighbour atoms. The EAM energy  $F(\rho)$  has the form

$$F(\rho) = -E_c \left[ 1 - \frac{\alpha}{\beta} \ln(\rho/\rho_e) \right] (\rho/\rho_e)^{\alpha/\beta} + \frac{1}{2} \sum_m \phi_e s_m \exp[-(p_m - 1)\gamma] \\ \times \left[ 1 + (p_m - 1)\delta - p_m \frac{\delta}{\beta} \ln(\rho/\rho_e) \right] (\rho/\rho_e)^{(\gamma/\beta)} \quad (5)$$

and the two-body potential  $\phi(r)$  is taken as

$$\phi(r) = -\phi_e [1 + \delta(r/r_{1e} - 1)] \exp[-\gamma(r/r_{1e} - 1)] \quad (6)$$

where  $p_m = r_m/r_1$ ,  $r_1$  is the distance to nearest neighbours,  $E_c$  is the cohesive energy,  $\alpha = (9B_e Q_e/E_c)^{1/2}$ ,  $B$  is the bulk modulus, and  $Q$  is the atomic volume. The subscript

e indicates evaluation at equilibrium. The parameters  $\beta$ ,  $\phi_e$ ,  $\delta$ , and  $\gamma$  are determined from fitting the atomic electron density, the unrelaxed vacancy formation, and the elastic constants.

We use equations (5) and (6) to describe the Ni(100) substrate and find that a satisfactory description of surface features such as the surface energy and the surface relaxations [16] can be obtained. Consider a slab of (100) surface, which consists of 36 Ni atoms and has a substitutional impurity or a vacancy existing in it. In order to study the interaction between H<sub>2</sub> and such an Ni substrate, we need to determine the functions  $F_H(\rho)$ ,  $\phi_{H-H}(R_{ij})$ ,  $\phi_{Ni-I}(R_{ij})$  and  $\phi_{H-I}(R_{ij})$ ; here subscript I denotes the impurity atoms, which are chosen as Cu and Pd in the present paper. The electron density for each metal atom is taken from the calculations of Clementi and Roetti [17] and is given as a sum of s and d contributions according to [10]

$$\rho(r) = N_s \rho_s(r) + (N - N_s) \rho_d(r) \quad (7)$$

where  $N$  is the total number of outer electrons;  $N_s$  is an empirical parameter that corresponds to the s-like content of the atomic electron density. The pair potential between atom A and atom B is obtained as [10]

$$\phi_{A-B} = \frac{Z_A(r)Z_B(r)}{r} \quad (8)$$

where  $Z(r)$  is the effective charge; A and B can be H, Ni, or impurity atom. The function  $F_H(\rho)$  is given by [10]

$$F_{H-H}(\rho) = b_1 \rho + b_2 + 1/(b_3 \rho + b_4) \quad (9)$$

where  $\rho$  is the electronic density of atoms in the range of the cut-off distance including Ni and another H atom. The two-body potential of H-H can be written as

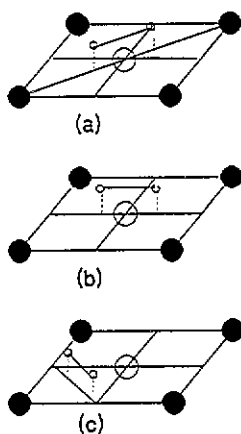
$$\phi_{H-H}(r) = E_{H_2}^{\text{tot}}(r) - 2F_H(\rho) \quad (10)$$

where  $E_{H_2}^{\text{tot}}$  is the total energy of the H<sub>2</sub> molecule in ground state.

The total energy for the H<sub>2</sub>/Ni system can be obtained by (3). The potential energy of H<sub>2</sub> on the Ni surface is obtained by  $E_{H_2/Ni}^{\text{tot}} - (E_{H_2}^{\text{tot}} + E_{Ni}^{\text{tot}})$ . In our calculations, the cut-off distance is taken as 4.0 Å which lies between the third- and fourth-neighbour distances of Ni.

### 3. Results and discussion

When an H<sub>2</sub> molecule approaches a metal surface, it can be adsorbed on different sites and the dissociation of H<sub>2</sub> can occur through various pathways. The cases we choose to investigate are shown in figure 1. The H-H axis is kept parallel to the substrate surface



**Figure 1.** Various dissociation pathways for  $H_2$  on the Ni(100) surface. The solid circles represent Ni atoms, the large empty circle represents a vacancy or impurity atom. The small empty circles are H atoms. The two H atoms extend (a) from an on-top site to bridge sites, (b) from an on-top site to centre sites, (c) from a bridge site to centre sites.

during the adsorption process. It is found that the activation barrier is lowest for this molecular orientation [18].

First we look at the adsorption of  $H_2$  on the perfect Ni(100) surface before we proceed to studying the impurity and vacancy effects. The calculated potential-energy surface is shown in figure 2. The dissociation path is that two H atoms extend from an on-top site to the adjacent bridge sites. It can be clearly seen that there is an entrance channel of adsorption for  $H_2$  approaching the substrate. When  $H_2$  is infinitely far away from Ni(100), the potential energy is zero (no interaction between  $H_2$  and Ni). As  $H_2$  approaches the surface, the H–H bond is gradually weakened while the H–Ni bonds begin to form. Finally, the molecule is adsorbed on the Ni surface in the form of two independent H atoms. In this dissociation process, there is a low barrier whose height is only 0.09 eV. The experimental result of Rendulic *et al* [4] is 0.06 eV, but the dissociation path is not known. The theoretical calculations performed by Harrison and Andersson [9] give a value of 0.1 eV, which is very close to our result. Then the H–H distance increases to 2.5 Å, the potential energy is lowest, and the two independent H atoms are adsorbed on two bridge sites on Ni(100). The corresponding H–Ni bond length is 1.73 Å and the adsorption heat is 1.12 eV. This is in good agreement with experimental measurements [19–21].

When a substitutional impurity atom Cu is present on the Ni(100) surface (we denote this as Ni(Cu)(100)), the corresponding potential-energy surface for  $H_2$  dissociation through the pathway of figure 1(a) is shown in figure 3. It is found that the activation barrier height is lifted from 0.09 eV to 0.51 eV due to the existence of the impurity atom Cu. The H–Cu bond length is 1.76 Å and the H–Ni bond length is 1.99 Å. The results shows that H–Ni bond is elongated by the Cu impurity. The adsorption heat for  $H_2$  on Ni(Cu)(100) is 0.70 eV. This is very close to the value for  $H_2$  adsorption on the Cu surface [22]. Both experimental and theoretical results [9, 23–26] for  $H_2$  on Cu surface indicate that this is an activated process. The barrier height is about 0.6–0.7 eV. From figure 3 we can see that the dissociative adsorption of  $H_2$  is remarkably influenced by the Cu impurity presented on the adsorption site. Figure 4 is the potential-energy surface for  $H_2$  adsorption on Ni(Pd)(100). The dissociation path is also shown in figure 1(a). It is found that the presence of a

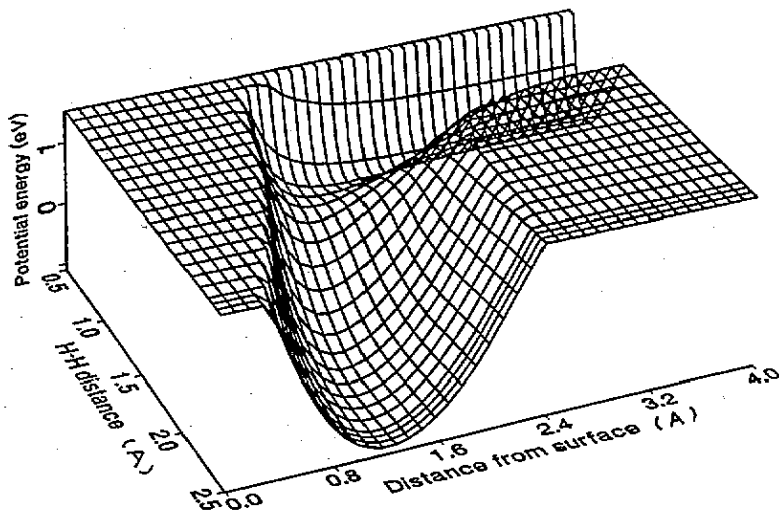


Figure 2. A two-dimensional representation of the interaction potential for H<sub>2</sub>/Ni(100). The dissociation pathway is the two H atoms extending from an on-top site to the adjacent bridge sites.

substitutional impurity atom Pd also lifts the activation barrier height (from 0.09 eV to 0.12 eV). The adsorption heat for H<sub>2</sub> on Ni(Pd)(100) is 1.15 eV, which is much closer to that on pure Ni(100). Compared with the Cu impurity, the influence of Pd on the H<sub>2</sub> adsorption is much less remarkable.

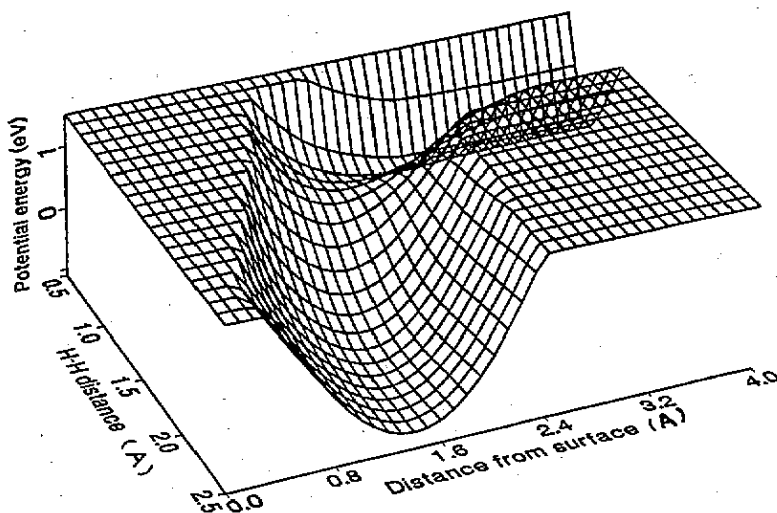


Figure 3. Potential-energy surface for H<sub>2</sub> on the Ni(Cu)(100) surface. The Cu atom is an impurity in the host Ni. The dissociation pathway is shown in figure 1(a).

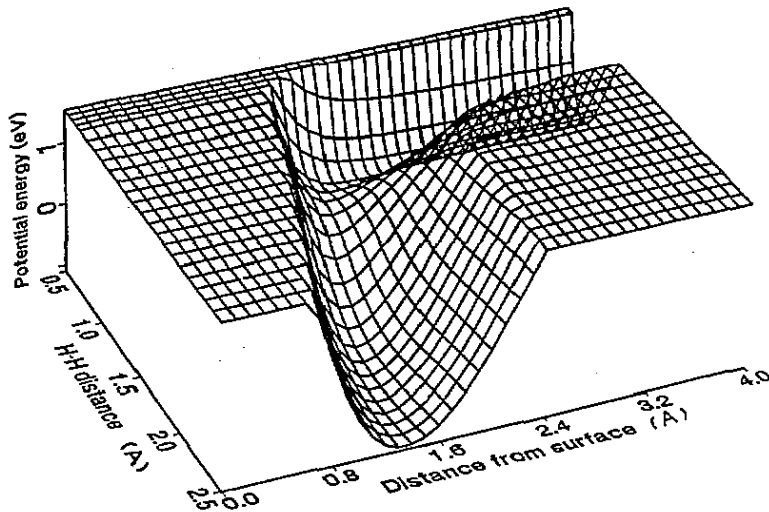


Figure 4. Potential-energy surface for  $H_2$  on the Ni(Pd)(100) surface. The Pd atom is an impurity in Ni. The  $H_2$  dissociation pathway is the same as in figure 1(a).

Table 1. Activation barriers ( $E_a$ ) for  $H_2$  dissociation on different substrate surfaces. Ni(100) with a Cu impurity atom is denoted as Ni(Cu)(100), Ni(100) with a Pd impurity atom is denoted as Ni(Pd)(100).  $E_a$  is in eV.

	On-top site to centre sites	Bridge site to centre sites	On-top site to bridge sites
Perfect Ni(100)	0.09	0.08	0.09
Perfect Pd(100)	0.13	0.11	0.12
Perfect Cu(100)	0.65	0.60	0.63
Ni(Pd)(100)	0.13	0.10	0.12
Ni(Cu)(100)	0.51	0.44	0.51

For  $H_2$  adsorption on other sites and dissociation through other pathways, we have calculated the activation barrier height, and the results are listed in table 1. The barrier height for  $H_2$  adsorption on the (100) surface of pure Ni, Pd, and Cu substrates are also listed for comparison. From table 1, we can see that for perfect Ni(100) the dissociation of the  $H_2$  molecule has almost the same barrier height for all three listed pathways, although that from bridge site to the adjacent centre sites appears the most favourable pathway. The presence of an impurity atom (Cu or Pd) causes an increase of the activation barrier height for all three dissociation pathways. The impurity effects on different pathways are somewhat different, and a different impurity has a different effect. It can be seen from table 1 that the influences of Cu are more significant than those of Pd.

The most important reason why the impurity atoms (Pd and Cu) can increase the activation barrier height of  $H_2$  dissociation on Ni surface is their different electronic configurations. The atomic electron densities used here are taken from calculations by Clementi and Roetti [17], which were based on single-determinant Hartree-Fock theory and therefore do not allow the proper mixing between given electronic configurations ( $3d^8 4s^2$ ,  $3d^9 4s^1$ ,  $3d^{10}$  for Ni, for example). In order to obtain the proper configuration of each metal

atom, Daw and Baskes [10] define an empirical parameter  $N_s$ , and the atomic electron density of each metal atom is given as a sum of s and d contributions according to (7). For a given metal  $N_s$  is determined by fitting the heat of solution of impurity atoms in it. The calculated values of  $N_s$  for Ni, Pd, and Cu are 0.85, 0.65, and 1.0, respectively. So the effective electronic configuration is  $3d^{9.15}4s^{0.85}$  for the Ni atom,  $4d^{9.35}5s^{0.65}$  for Pd, and  $3d^{10}4s^1$  for Cu. Harris and Andersson [9] pointed out that the d holes (unfilled d bands) can open up an escape route for the s electrons as the H<sub>2</sub> molecule penetrates the outer tails of the wave functions of the metal electrons. This s-d electron transfer dramatically reduces the Pauli repulsion between an H<sub>2</sub> molecule and a metal substrate. The repulsion is responsible for the activation barrier. Therefore, the bigger the d hole is, the lower the barrier height will be. Here the unfilled fraction of the d band for Ni is 0.85, that for Pd is 0.65, and that for Cu is 0.0, so Ni gives the lowest barrier and Cu gives the highest one. If Cu or Pd were present in the host Ni substrate as an impurity atom, it would certainly bring some characteristics of Cu or Pd and the activation barrier height for H<sub>2</sub> dissociation taking place near the impurity site would be increased.

Of course in real adsorption cases, the impurity atom may not be at the site we have assumed. The variations of the impurity position are shown in figure 5. For each possible impurity position (here we just take account of the Cu impurity), we calculated the activation barrier and the adsorption heat for H<sub>2</sub> dissociation from the on-top site to the adjacent bridge sites. The results are listed in table 2. It is found that as the impurity atom moves away from the adsorption site, i.e. position 1 in figure 5, the effects decrease rapidly. When Cu is located on site 4 or site 5, the adsorption of H<sub>2</sub> is just like that on pure Ni(100); the effect of the impurity atom is almost negligible, i.e. the impurity atom can only affect the adsorption of H<sub>2</sub> close to itself. This is because the d bands are relatively narrow and the d wave functions are relatively well localized about the metal atoms. So, near the impurity (Cu) site only, the d orbitals are fully occupied and the s-d transfer is reduced.

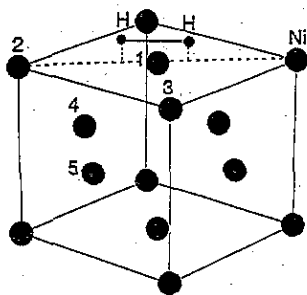


Figure 5. Different impurity sites on the Ni(100) surface.

Table 2. Activation barriers ( $E_a$ ) and adsorption heat ( $E_{ad}$ ) for H<sub>2</sub> dissociation on the Ni(100) surface corresponding to an impurity (Cu) at different sites.

Site	1	2	3	4	5
$E_a$ (eV)	0.51	0.20	0.19	0.09	0.09
$E_{ad}$ (eV)	0.70	0.97	0.97	1.15	1.15



The potential-energy surface for  $H_2$  approaching a vacancy in Ni(100) is shown in figure 6. The dissociation pathway we choose to investigate is the same as in figure 1(a). It can be seen that an  $H_2$  can approach the surface, experiencing a very slight repulsion, then surmount a low barrier (0.07 eV) and dissociate into two independent H atoms. There are two adsorption sites: one is on the surface (the distance from the surface is zero), the H-H bond length is 1.8 Å, and the H-Ni bond is 1.6 Å; the other is above the surface, the H-H distance is 2.5 Å, and the H-Ni bond length is 1.8 Å. The two adsorption sites have equal adsorption heat (1.17 eV). For  $H_2$  dissociation on Ni(100) through other pathways (figure 1(b) and figure 1(c)), the calculated barrier height is 0.08 eV. Comparing with the perfect Ni(100) (figure 2), we can conclude that the existence of vacancy reduces the activation barrier height and provides more adsorption sites. This can be easily understood if we carefully investigate the process of  $H_2$  adsorption on metal surfaces. The bond energy of the  $H_2$  molecule is 4.6 eV, which is approximately twice the bond energies of most metal-H dimers. In order to compete with the H-H interaction, the metal-H interaction must have a value of about 2 eV, which requires that the proton of H be very close to the metal atom. As the  $H_2$  molecule gradually penetrates the outer tails of the wave function of the metal electrons, the Pauli repulsion between the s electrons of the metal atom and the 'occupied'  $H_2$   $1\sigma_g$  orbital prevents the H atoms from approaching close enough to the Ni substrate atoms. Once the  $H_2$  molecule surmounts this barrier, the H-H interaction is rapidly weakened and the H-Ni bond is formed. The presence of a vacancy in the Ni surface provides a hole of electron density, which acts as an entrance route for  $H_2$  approaching the substrate. Therefore the  $H_2$  can approach close to Ni atoms along this path experiencing lower Pauli repulsions.

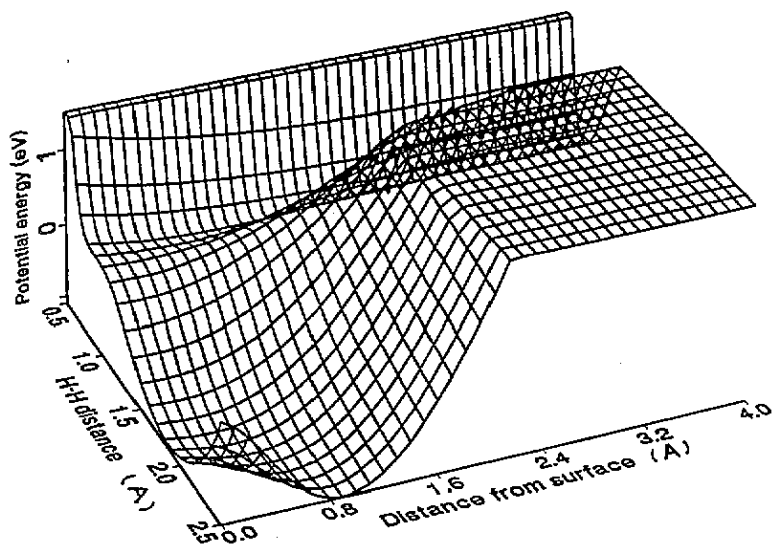


Figure 6. Potential-energy surface for  $H_2$  on the Ni(vac)(100) surface. There is a vacancy on the Ni surface. The  $H_2$  dissociation pathway is the same as in figure 1(a).

#### 4. Summary

In the present paper, we have investigated the effects of impurities and vacancies on the dissociative adsorption of H<sub>2</sub> molecule on the Ni(100) surface. From the calculations, the following can be concluded.

(a) The presence of the substitutional impurity atom (Cu or Pd) increases the activation barrier height. The effect of Cu is more significant than that of Pd. As the impurity atom moves away from the adsorption site, the corresponding influence on H<sub>2</sub> dissociation decreases rapidly.

(b) The vacancy can reduce the barrier height and provide more adsorption sites.

The above conclusions provide insights into poisoning or promoting the dissociation reactions of H<sub>2</sub> on Ni(100). The presence of impurity atoms such as Cu or Pd investigated here impede the H<sub>2</sub> molecule's dissociation on the Ni surface by increasing the activation barrier height. The reason is that they have fewer unfilled d orbitals. It can be expected that the fully occupied d band atoms such as Ag and Au may also poison H<sub>2</sub> dissociation on the Ni substrate. If the H<sub>2</sub> molecule approaches close to the substrate and experiences smaller Pauli repulsion, the dissociation of H<sub>2</sub> is promoted because the activation barrier is lower. A vacancy in the surface presents an entrance path for H<sub>2</sub> approaching the substrate; therefore, it promotes the dissociation of H<sub>2</sub>.

#### Acknowledgments

One of the authors (J Xie) greatly thanks Professor S G Davison and Professor W K Liu (University of Waterloo, Canada) for suggesting the present topics of diatomic molecule-surface interactions. This work is supported by the National Science Foundation of China.

#### References

- [1] Robota H J, Vielhaber W, Lin M C, Segner J and Ertl G 1985 *Surf. Sci.* **155** 101
- [2] Sternruck H P, Rendulic K D and Winkler A 1985 *Surf. Sci.* **154** 99
- [3] Martensson A-S, Nyberg C and Anderson S 1986 *Phys. Rev. Lett.* **57** 2045
- [4] Rendulic K D, Winkler A and Karner H 1987 *J. Vac. Sci. Technol. A* **5** 488
- [5] Lee Chyuan-Yih and DePristo A E 1987 *J. Vac. Sci. Technol. A* **5** 485
- [6] Sigban P E M, Blomberg M R A and Bauschlicher C W 1984 *J. Chem. Phys.* **81** 2103
- [7] Norskov J K 1989 *J. Chem. Phys.* **90** 7461
- [8] Darling G R and Holloway S 1990 *J. Chem. Phys.* **93** 9145
- [9] Harris J and Andersson S 1985 *Phys. Rev. Lett.* **55** 1583
- [10] Daw M S and Baskes M I 1984 *Phys. Rev. B* **29** 6443
- [11] Foiles S M, Baskes M I and Daw M S 1986 *Phys. Rev. B* **33** 7983
- [12] Foiles S M 1985 *Phys. Rev. B* **32** 7685  
Daw M S 1988 *Phys. Rev. B* **39** 7441
- [13] Johnson R A 1989 *Phys. Rev. B* **39** 12554
- [14] Adams F B and Foiles S M 1990 *Phys. Rev. B* **41** 3316
- [15] Mei J, Davenport J W and Fernando G W 1990 *Phys. Rev. B* **43** 4653  
March N H 1986 *Chemical Bond Outside Metal Surfaces* (New York: Plenum)
- [16] Xie J J and Jiang P 1993 unpublished
- [17] Clementi E and Roetti C 1974 *Atomic Data and Nuclear Data Tables* vol 14 (New York: Academic) Nos 3 and 4
- [18] Reichtien J-H, Harder R, Hermann G and Snowdon K J 1992 *Surf. Sci.* **272** 240

- [19] Melius C F, Studen R H and Noell J O 1982 *Phys. Rev. Lett.* **48** 1429
- [20] Christmann K, Schober O, Ertl G and Neumann M 1974 *J. Chem. Phys.* **60** 4528
- [21] Louie S G 1979 *Phys. Rev. Lett.* **42** 476
- [22] Alexander C S and Pritchard J 1972 *J. Chem. Soc., Faraday Trans. I* **68** 202
- [23] Campbell J M and Campbell C T 1991 *Surf. Sci.* **259** 1
- [24] Hayden B E and Lamont C L A 1991 *Surf. Sci.* **243** 31
- [25] Harris J 1989 *Surf. Sci.* **221** 335; 1988 *Appl. Phys. A* **47** 68
- [26] Rendulic K D 1992 *Surf. Sci.* **272** 34