

# Dissociation and atom recombination of H<sub>2</sub> and D<sub>2</sub> on metallic surfaces: A theoretical survey

M. Cacciatore and G.D.Billing(°)

CNR-Centro di Studio per la Chimica dei Plasmi, Dipartimento di Chimica  
Universita di Bari, v.Orabona 4, 70126 Bari (Italy)  
(°)Chemistry Laboratory III, H.C.Ørsted Institute, University of Copenhagen  
2100 Copenhagen ( Denmark )

**Abstract:** The inelastic and dissociative chemisorption of H<sub>2</sub> (v,j) and D<sub>2</sub> (v,j) on Cu surfaces has been studied in a wide range of collisional kinetic energies below and above the activation barriers to dissociation. The dynamic calculations have been performed within a fully multi-dimensional semiclassical and a two-dimensional quantum wave packet approach. The important aspects concerning the different behaviours of vibrationally excited molecules coming from the gas-phase and dissociating on the surface are presented and discussed. The hydrogen atom recombination via Eley-Rideal mechanism has been also studied and the relevant rate coefficient as a function of the translational temperature of the gas-phase atom has been calculated.

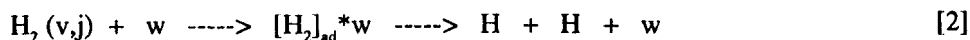
## INTRODUCTION

In the last few years a great deal of theoretical and experimental work has been done on the dissociative chemisorption of H<sub>2</sub> and D<sub>2</sub> on metal surfaces. This interest has been stimulated not only by fundamental questions concerning the interaction dynamics (1) but also because of the key role played by heterogeneous processes in the field of classical catalysis (2) as well as in the field of non-equilibrium hydrogen kinetics, including plasma-wall interactions, chemical vapour deposition (3) and nuclear reactors (4). Low-energy thermal collisions on the wall ( w ) can lead to a variety of energetic activation/deactivation processes, the simplest possible inelastic and reactive processes are:

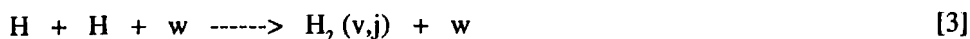
-- vibrational and rotational relaxation in inelastic collisions:



-- dissociative chemisorption when a molecule interacts in a specific surface site and then dissociates with the two atoms adsorbed or propagating in the gas-phase:



-- hydrogen atom recombination ( associative desorption ):



Processes [1,2,3] can be so efficient that they compete successfully with the several others gas-phase collisional processes (involving hydrogen atoms, molecules, and electrons ) (5) in determining the concentration of the active species, H atom and vibrationally excited molecules, in the wall region as well as in the volume domain. The importance of these processes in the overall hydrogen kinetics very much depends on the operative conditions of the chemical reactor (6), that is its geometry and gas pressure, and obviously on the catalytic nature of the walls.

For noble metals, Cu (1) and low-index Ni and Fe surfaces (7,8) the H<sub>2</sub> chemisorption is energetically activated, and the activation energy E<sub>a</sub> must be supplied to the molecule for the dissociation to take place. Consequently, the dissociation probabilities are small. On transition metals Pd, W, and high index plane Ni Pt, the dissociative chemisorption is almost spontaneous, with high sticking (dissociation) probabilities. The nature of the activation barrier and how it correlates with the electronic structure of H<sub>2</sub> and the substrate is very complex and not completely understood. The main factor is the closed shell nature of the H<sub>2</sub> electronic

structure and the consequent Pauli repulsion which arises when the molecule interacts with the metal electrons (9). The changing in the *sp* and *d* band density in proximity of the Fermi level according to the *d*-character of the metal is responsible for the progressive suppression (with some exception) of the repulsive barrier when going to the left from the noble metal Cu group (10).

The energetic of the dissociative interaction of H<sub>2</sub> on surfaces is generally discussed by a one-dimensional representation of the H/H<sub>2</sub>-metal potential energy surface (PES) as a function of the particle distance from the surface (considered as the reaction coordinate). Instead, it turns out that there is a distribution of barriers, with different E<sub>a</sub>, depending on the chemisorption surface site. The dependence of the sticking probability on the surface coverage and surface morphology is the macroscopic manifestation of the multidimensional character of the PES. There is much experimental evidence that the hydrogen dissociation occurs preferentially on stepped surfaces (1,11,12). Thus, the sticking probability on Pt is in the range 10<sup>-4</sup> on Pt(111) to 0.01 - 0.1 on stepped surfaces with steps (13).

A very interesting aspect of the activated chemisorption of H<sub>2</sub> on metals is that the vibrational energy, possibly together with the rotational energy, can be an efficient energy source for overcoming the repulsive barrier. The difficulty in preparing the molecule in a specific initial vibrational state to evidence the vibrational energy dependence of the dissociation probability of H<sub>2</sub> on Cu surfaces, gave rise to a number of misunderstandings on the determination of the activation energy (14), until the very recent determinations made in seeded molecular beam experiments (1). The critical dependence of the dissociation probability on the vibrational quantum number was predicted in early theoretical calculations and subsequently confirmed by more refined classical (15), semiclassical (16) and quantum mechanical studies (17,18)

Process [3] has also attracted considerable attention due to its importance both for the formation of vibrationally excited molecules, and as an effective loss process of hydrogen atoms. In the reaction a considerable amount of energy ΔE<sub>ex</sub> is liberated which can be partitioned between the translational and the internal motions of the desorbing H<sub>2</sub>. Translationally hot D<sub>2</sub> molecules after atomic permeation on Pd and Cu surfaces have been detected (19) and a possible mechanism for the dynamics has been suggested.

Process [3] can occur via two possible (extreme) mechanisms, i.e. the Langmuir-Hinshelwood (LH) mechanism and the Eley-Rideal (ER) mechanism. In the former case two adsorbed atoms recombine, while according to the ER mechanism the hydrogen atom approaching the surface from the gas phase reacts with the ad-atom. For the LH case, ΔE<sub>ex</sub> = E<sub>D</sub> - 2\*E<sub>H</sub> - ΔE<sub>ad</sub>, where E<sub>D</sub> is the dissociation energy of H<sub>2</sub>, E<sub>H</sub> the hydrogen adsorption energy and ΔE<sub>ad</sub> is the (generally small) energy loss to the wall. In the other case the available energy for vibrational excitation is higher, ΔE<sub>ex</sub> = E<sub>D</sub> - E<sub>H</sub> - ΔE<sub>ad</sub>. Depending on the E<sub>H</sub> and E<sub>D</sub> values, H<sub>2</sub> can be populated up to a maximum *v*' value (*v*'<sub>max</sub> ~ 5 for the ER process)

The 'direct' observation of surface processes in real physical situations is very difficult. Although somehow hidden, there is much 'indirect' experimental evidence on the importance of hydrogen atom recombination on the wall, virtually in all type of H and H<sup>+</sup> sources (20).

Suprathermal vibrational distributions have been observed in cell (21) up to *v*'=5, consistently with the ER mechanism, and up to *v*'=9 (22). This later experiment has aroused the (intriguing) question of which mechanism other than ER reaction is responsible for the population of H<sub>2</sub> (*v*'>5). Similar determinations have been performed in volume plasma sources (23,24,25). On the basis of a simple kinetics modelling of the measured hydrogen atom density, the recombination coefficient was estimated to be P=0.12 (23), most likely in the interval 0.05+0.2. A more realistic and complex kinetic modelling of the hydrogen atom production in these sources would require a higher P value, P=0.5 (26). Unfortunately, the exact nature of the walls, most probably tungsten covered copper surfaces, is not known in these experiments. Recently, indirect observations of the hydrogen atom recombination on the wall have been made in afterglow and RF discharges (27a,b) (28). Theoretical quantum models of the ER hydrogen recombination have been developed in Ref.(29,30).

In the following sections we report on our recent investigations on the dissociative chemisorption of vibrationally excited H<sub>2</sub> and D<sub>2</sub> molecules on Cu surfaces (16,31,32). The most important results obtained in these works will be presented and discussed. New results on the dynamics of the hydrogen atom recombination in the ER processes will be presented in the last section of the paper. The molecular dynamics calculations have been performed within the semiclassical and the two-dimensional wave packet approaches which allowed us to take into account the most important features of the molecule/surface interactions, including the dynamics of the phonons and electron hole-pairs of the substrate.

## DISSOCIATION AND VIBRATIONAL RELAXATION OF H<sub>2</sub>/D<sub>2</sub> ON Cu: HIGH ENERGY COLLISIONAL REGIME.

As ever in molecular dynamics calculations, the first step is the search for a sufficiently accurate potential energy surface. Unfortunately a unique PES does not exist even for such an elementary collisional system. Different electronic structure calculations (33,34,35) give different values for the activation barriers, ranging from 0.7eV to 1.8eV. The PES used in our early study (16,31) was obtained as an analytical fit to ab initio SCF-CI cluster calculations (33). The global PES (31) exhibits energy barriers to chemisorption which are sensitive to the surface absorption site, the H-H bond distance and to the molecular orientation. Thus, the barrier height is 0.93eV for H<sub>2</sub> approaching the surface perpendicularly on the on top site, while the on top parallel configuration is less favoured with E<sub>a</sub> around 1.76eV. The energetic barrier is located slightly into the exit channel with H<sub>2</sub> in a stretched bond configuration. Therefore, the PES points towards a dissociation mechanism assisted by the vibrational and rotational motion of H<sub>2</sub>. We have performed semiclassical trajectory calculations on this PES. Details of the method have been given in Ref.(31,36). The most important feature of the method is the definition of an effective hamiltonian which couples the translational and internal motion of H<sub>2</sub>, treated classically, with the quantum phonon modes of the Cu surface. This allows us to evaluate the energy transfer between the chemical system and the solid substrate.

The hamiltonian is given by:

$$H_{\text{eff}} = \frac{1}{2} \sum_{i\alpha} P_{i\alpha}^2 + V_{\text{H}_2}(r) + V_0(X_i, Y_i, Z_i) + \sum_{k=1}^M V_k^{(1)}(X_i, Y_i, Z_i) \eta_k(t, T_s)$$

where the first term is the kinetic energy of the two H atoms in the gas phase,  $V_{\text{H}_2}$  is the intermolecular potential.  $V_0$  is the static potential between the H<sub>2</sub> and the surface atoms,  $V_k^{(1)}$  is the time dependent external force which drives the motion of the k.th phonon mode.  $\eta_k$  is the phonon excitation strength due to the H<sub>2</sub>-phonon interaction. The crystal surface consists of about 89 lattice atoms displayed in three layers. The top layer is in the (X,Y) plane, Z is the axis normal to the surface plane. In Fig. 1 we have reported the dissociation probability  $P(v)$  for vibrationally excited D<sub>2</sub> molecules,  $v=1,5$  and  $j=0$ , as a function of the collision energy  $E_{\text{kin}}$ . Similar data can be found in Ref.(31) for the dissociation of H<sub>2</sub> ( $v,j$ ).

There is a significant effect of the vibrational energy on the dissociation probability, in agreement with the experimental observations made at lower collisional energies (37,38). This effect, which has never been considered in kinetic modelling, could have important consequences in hydrogen plasmas where a significant fraction of H<sub>2</sub> and D<sub>2</sub> is formed in vibrationally excited levels via electron-molecule collisions.

The vibrational quantum number dependence of the dissociation probability is a consequence of the PES topology assumed in the our calculations, i.e. the lowering of the activation barriers with the increase of the D-D bond distance. There is also another 'dynamical' effect which enhances the dissociation of vibrationally excited molecules, that is the energy exchanges between the translational and the vibrational motions of the molecule. In fact, the analysis of the dissociative trajectories shows that the dissociation takes place through a complex translation-to-vibration exchange mechanism. This is shown in Fig. 2 where the vibrational (dotted

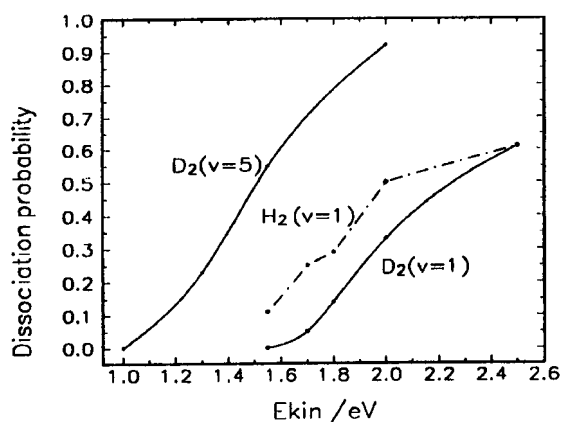


Fig. 1 Semiclassical dissociation probability for D<sub>2</sub>/H<sub>2</sub> on Cu

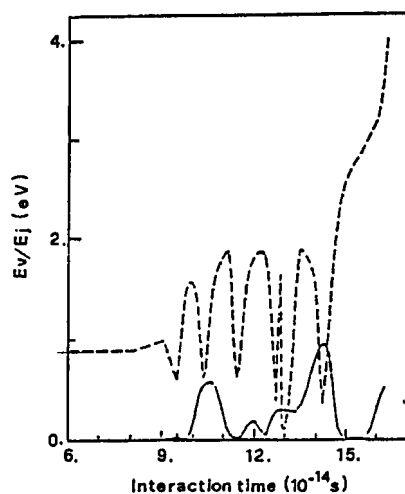


Fig. 2 Time evolution of the vibrational (---) and the rotational energy of D<sub>2</sub> dissociating on Cu

line ) and rotational energy of  $D_2(v=2,j=0)$  approaching the copper surface is reported for a typical dissociative trajectory as a function of the collision time. The trajectory calculations also show that there is an isotope effect on dissociation (see Fig. 1). In the classical picture, the smaller dissociation probability of  $D_2$  with respect to  $H_2$  is primarily due to the higher energy loss to the surface phonons ( see Table 3 of Ref. 32 ).

In Fig. 3 we have reported the final state vibrational distribution of the reflected  $D_2$  molecules hitting the surface in the initial states ( $v=1, j=0$ ) and  $E_{kin}=1.5, 1.75, 2.0, 2.25, 2.5eV$ . For energies below 1.5eV the surface is almost inert, the molecules are scattered virtually elastically in their initial vibrational state. At higher collision energies, the molecules are more efficiently quenched and the population of the three neighbouring states increases. Although of high accuracy, the ab initio PES used in this work is rather inert to dissociation. In fact, in later experimental determinations (37,38) the dissociation energy threshold for  $D_2$  ( $v=0$ ) was found around  $E_{kin}=0.3eV$ . Fully classical trajectory calculations (15) on a different PES with lower chemisorption barriers give dissociation probabilities much higher than that found in our work.

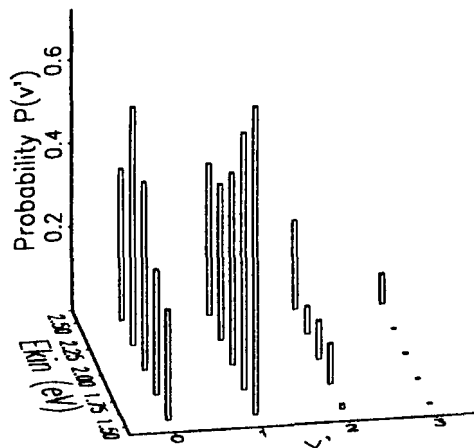


Fig.3 Relative vibrational distribution for inelastically reflected  $D_2$  molecules ( process [1] )

## DISSOCIATION IN THE LOW ENERGY COLLISIONAL REGIME

Quantum tunnelling effects through the chemisorption are important at collisional energies below and near the barrier heights (17,18). Therefore we have estimated the dissociation probability for  $D_2/H_2$  on Cu using a semiclassical two-dimensional wave packet approach. According to this method the vibrational coordinate  $r$  is quantised, together with the component of the translational motion of  $D_2$  along the tunnelling coordinate  $Z$ . The remaining  $X, Y$  translational components and the polar angles  $\theta$  and  $\phi$  are treated classically as in the previous calculations. The wave function  $\Psi(r, Z, t)$  of the quantum part of the system is written as a product of: the Morse wave function of the molecule in a given vibrational state, the wave packet in the  $Z$ -coordinate and the phonon wave function. The time evolution of the total wave function is then obtained by simultaneously solving the  $t$ -dependent Schrödinger equations for the  $r$  and  $Z$  coordinates

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2M} \frac{\partial^2}{\partial Z^2} + V_0(Z, r, t) + \sum_{k=1}^M V_k^{(1)}(Z, r, t) \eta_k(t, T_s)$$

and the Hamilton equations for the rotational and translational motion in  $X$  and  $Y$  directions. The computational effort needed with such complex dynamical model is very high, so that the dissociation probability has been calculated at only few kinetic energies. The tunnelling probabilities on the PES used in our previous calculations, see previous section, are too small compared to the experimental values (37). We have therefore modified the original PES to obtain a potential surface with lower activation barriers.

Figure 4 is a contour plot of the interaction potential of  $H_2$  approaching the surface in a parallel orientation on the on top site. After surmounting a small physisorption barrier in the entrance channel, the molecule is chemisorbed in the potential well A. The chemisorption well for the dissociated H atoms is in C, while the energy barrier between  $H_2$  and  $H + H$  is in point B where the H-H bond distance for the 'activated' molecule is around 1.8Å. The barrier height is about 0.4eV in this interaction site. In Fig. 5 we have reported the dissociation probabilities for  $D_2$  ( $v=0, j=0$ ) at three collision energies. The agreement with the experimental values ( crosses ) is good.

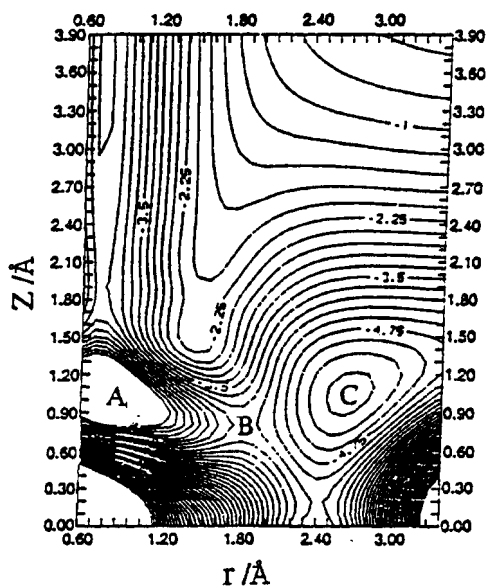


Fig. 4 Potential contour map for D<sub>2</sub> interacting parallel to on top Cu site

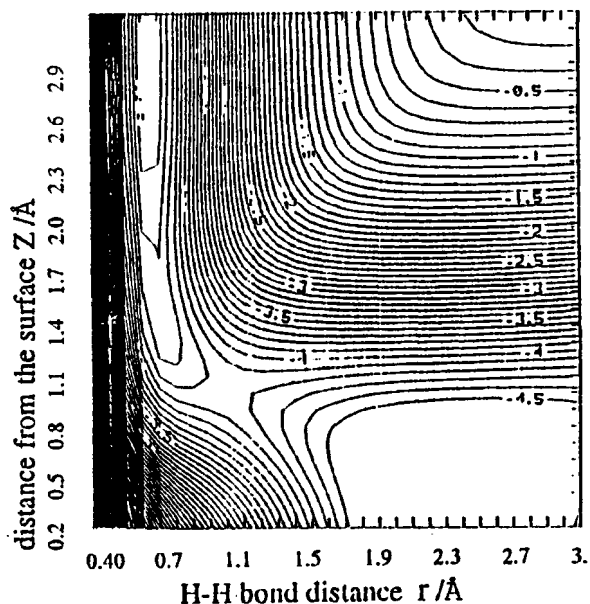


Fig. 6 EDIM contour map for H<sub>2</sub> in the bridge parallel site of Cu(001)

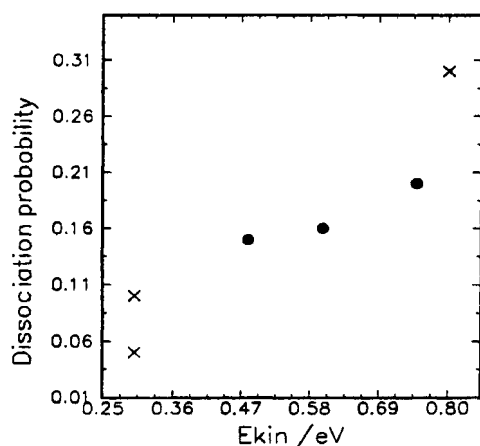


Fig. 5 Tunnelling dissociation probability for D<sub>2</sub>( $v=0, j=0$ )

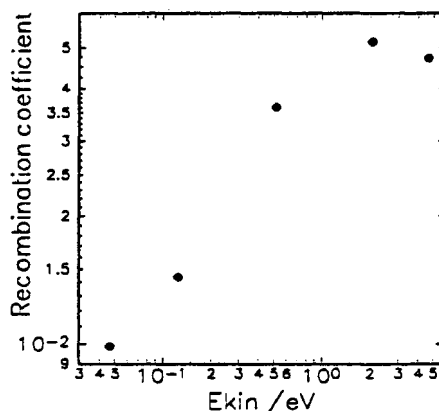


Fig. 7 Hydrogen recombination probability  $P_{ER}$

### HYDROGEN ATOM RECOMBINATION ON Cu.

The dynamics of the hydrogen atom recombination on Cu(111) has been studied within the semiclassical trajectory method. The rate determining step in the ER mechanism is simulated in the calculations. In the model calculations we have assumed a three-dimensional Cu with H<sub>ad</sub> placed on the top layer in thermal equilibrium with the surface (the surface temperature is  $T_s=300\text{K}$ ). Thus the atom is given an initial momentum  $p_z$  in the negative Z direction towards the surface. The atom in gas-phase strikes the surface with a given kinetic energy and initial polar angles  $(\theta, \varphi)=(0,0)$ . The initial position coordinates are randomly chosen in the aiming area A within the unitary cell. Then the incoming H atom sees a surface coverage of 1 atom/Å ( $A=9.6 \text{ \AA}^2$ ).

An important conclusion that has emerged in our study as well as in other theoretical studies (32), is that a reliable ab initio PES for the H/H<sub>2</sub>-Cu system is essentially unavailable at present, and therefore one has to rely on semiempirical PES combining ab initio calculations with the experimental data on the chemisorbed molecule. We have used the embedded diatom in molecules (EDIM) method (39) for constructing a new PES (see Fig. 6). The hydrogen dissociation within the wave packet approach has been calculated on this

new PES (40). Compared to the  $P_{\text{dis}}$  reported in the previous section, the new results are in slightly better agreement with the experimental results. Here we present the semiclassical results obtained for the recombination process on the EDIM surface. Figure 7 shows the recombination probability  $P_{\text{ER}}$  as a function of the kinetic energy  $E_{\text{kin}}$  of the gas atom. There is a fast increase of  $P_{\text{ER}}$  with  $E_{\text{kin}}$ , and this is a consequence of the existence of the energetic barrier for molecular desorption. Quantum calculations on a PES without activation barrier for recombination give a greater recombination coefficient which is almost constant with the collision energy (29,30).

The relative probability distribution  $P(v)$  of the back scattered  $\text{H}_2$  molecules has been plotted in Fig. 8 for five values of the kinetic energy of the gas atom,  $E_{\text{kin}} = 0.047, 0.129, 0.524, 2.056, 4.622$  eV. The results show that the desorbing molecules are formed in highly vibrationally excited levels, up to  $v=12$ . Molecules in the very highly vibrational states are formed in the gas phase between the incoming H atom and the H ad-atom back-scattered from the surface.

The influence of the chemisorption site on the ER recombination process has not been considered in this work. However, a more complete investigation on this subject can be found in Ref. (41) where the recombination of carbon atoms with oxygen atoms chemisorbed on Pt(111) has been studied in more details. A small surface temperature effect on the recombination probability was found in this work, as it is expected for the ER mechanism.

The ER reaction rate constant can be obtained from the flux of the hydrogen atoms hitting the surface. Thus, from the gas kinetic theory, and for the geometry assumed in the simulation we have:

$$n_{\text{H}_2} = \frac{p}{kT} A \left( \frac{1}{2\pi mkT} \right)^{1/2} \int P_{\text{HR}}(E_z) \exp\left(-\frac{E_z}{kT}\right) dE_z = \frac{p}{kT} K$$

where  $n_{\text{H}_2}$  is the number of H atoms which recombine per unit time on the surface area  $A$ .  $E_z$  is the energy normal to the surface,  $p$  is the gas pressure. The rate constant  $K(\text{cm}^3 \text{s}^{-1})$  is reported in Fig. 9 at different temperatures.

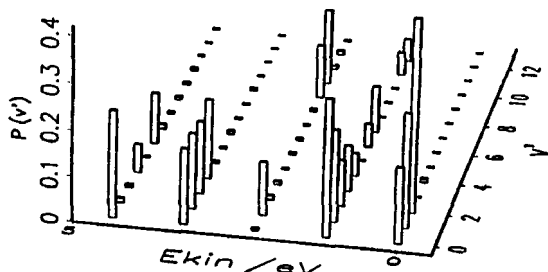


Fig. 8 Relative probability distribution  $P(v')$  for desorbing  $\text{H}_2$  molecules

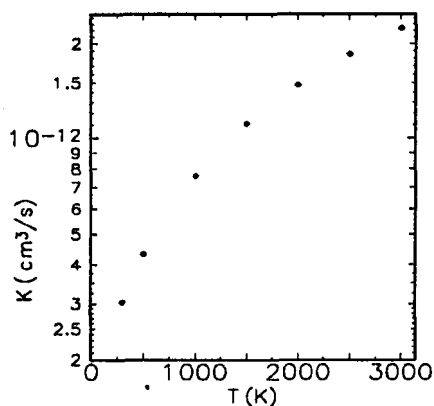


Fig. 9 Rate constant for hydrogen atom recombination on Cu

## CONCLUSIONS

The dissociative  $\text{H}_2/\text{D}_2$  chemisorption and the hydrogen atom recombination on Cu surfaces has been studied within a semiclassical and a semiclassical wave packet approaches which have been shown to be of great help in interpreting several atom/molecule-surface interaction phenomena. In fact, the multi-dimensional feature of the system is retained in the simulations, thus the atom/molecule coming from the gas phase is allowed to propagate on the surface before reacting in a specific site. Although a fully reliable PES for the  $\text{H}/\text{H}_2$ -Cu interaction is not available at present, two main conclusions can be drawn from our study: a) the dissociation probability for  $\text{H}_2/\text{D}_2$  in the  $v=0$  state is quite large even at low collisional energies. Furthermore, the dissociation probability increases rapidly for vibrationally excited molecules.

b) consequently,  $\text{H}_2$  molecules from ER reaction on the wall are formed in highly vibrationally excited states.

## REFERENCES

1. B.E.Hayden in :*Dynamics of gas-surface interactions*, eds. C.T.Rettner and M.N.R.Ahsfold, p.137, The Royal Society of Chemistry, Cambridge (1991).
2. Z.Knor in: *Catalysis*, vol.3,Eds. M.Boudard and J.R.Anderson, p.23, Springer, Berlin (1982)
3. J.C.Angus and C.C.Hayman *Science* **241**,913 (1988)
4. . see: '*Production and Neutralization of Negative Ions and Beams*', A.Hershcovitch Ed., AIP Conf.Proc. New York (1994)
5. M.Cacciatore, M.Capitelli and R.Celiberto *Nuclear Fusion, Suppl. on Atomic, Molecular and Plasma-wall Interactions Data for Fusion*, Ed. R.K.Janev, **2**, 65 (1993)
6. M.Boudard *Kinetics of chemical processes*, Prentice Hall (1968)
7. H.J.Robota, W.Viehlander, M.C.Lin, J.Segner and G.Ertl *Surface Sci.* **155**,101 (1985)
8. H.F.Berger, E.Grösslinger and K.Rendulic *Surface Sci.* **313** (1992)
9. J.Harris, S.Holloway, T.S.Rahaman and K. Yang *J.Chem.Phys.* **89**, 4427 (1988)
10. J.K.Nørskov and P.Stolze *Surface Sci.* **189/190**, 91 (1987); P.Nordlander, S.Holloway and J.K.N Nørskov *Surface Sci.* **136**,59 (1984)
11. R.S.Polizzotti and G.Ehrlich *J.Chem.Phys.* **71**,259 (1979)
12. P.W.Tamm and L.D.Schmidt *J.Chem.Phys.* **55**, 4253 (1971)
13. P.Poelsena, K.L.Lenz, S.L.Bernasek, I.K.Vorheij and G.Comsa *Surface Sci.* **189/190**, 431 (1987)
14. C.T.Rettner, H.A.Michelsen and D.J.Auerbach *Faraday Discuss.* **96**, 17 (1993 )
15. A.Forni, G.Wiesenekker, E.J.Baerends and G.F.Tantardini *Int.J.Quant.Chem.* **52**, 1067 (1994)
16. M.Cacciatore, M.Capitelli and G.D.Billing *Surface Sci.* **217**, L391 (1989)
17. J.Harris, S.Holloway, T.S.Rahman and K. Yang *J.Chem.Phys.* **89**, 4427 (1988)
18. S.Kuchenhoff, W.Brenig and Y.C.Chiba *Surface Sci.* **245**,389 (1991)
19. G.Comsa and R.David *Surface Sci.* **177**, 77 (1982)
20. A.W.Kley in : '*Production and Neutralization of Negative Ions and Beams*', Ed. A. Hershcovitch, AIP Conf.Proc.N°210, p.3, New York (1990)
21. P.J.Eenshuijstra, J.H.M.Bonnie, J.Loss and H.J.Hopman *Phys.Rev.Lett.* **60**, 341 (1988)
22. R.Hall, I.Cadez, M.Landau, F.Pichou and C.Sherman *Phys.Rev.Lett.* **60**, 337 (1988)
23. P.J.Eenshuijstra, R.M.A.Heeren, A.W.Klein and H.J.Hopman *Phys.Rev.* **A40**, 3613 (1989)
24. M.Pealat, J.P.taran, M.Bacal and F.Hillion *J.Chem.Phys.* **82**, 11943 (1985)
25. G.C.Stutzin, A.T. Yang, A.S.Schlachter, K.N.Lang and W.B.Kunkel *Chem.Phys.Lett.* **155**, 475 (1989)
26. P.Berlemont, D.A.Skinner and M.Bacal in: Proc.5th. Int. Sym. on Negative Ion and Beams, AIP Conference Proc. N°, Ed. A. Hershcovitch, p.77 , New York (1994)
27. (a) L.St-Onge and M.Moisan *Plasma Chem.Plasma Process.* **14**, 87 (1994); (b) D.K.Otorbaev, M.C.M. van de Sanden and D.C.Schram *Plasma Sources Sci.Technol.* **4**,293 (1995)
28. J.Deson, F.Halona, C.Lalo, A.Rousseau and V.Veniard *J.Phys.* **D27**, 2320 (1994)
29. P.Kratzer and W.Brenig *Surface Sci.* **254**, 275 (1991)
30. B.Jackson and M.Persson *J.Chem.Phys.* **96**, 2378 (1992)
31. M.Cacciatore and G.D.Billing *Surface Sci.* **232**, 35 (1990)
32. G.D.Billing and M.Cacciatore *Faraday Discuss.* N° **96**, 33 (1993)
33. P.Madhavan and J.L.Whitten *J.Chem.Phys.* **77**, 2673 (1982)
34. J.Harris and S.Andersson *Phys.Rev.Lett.* **55**, 1583 (1985)
35. K.Johansson *Surface Sci.* **104**, 510 (1981)
36. G.D.Billing. *Chem.Phys.* **74**, 143 (1983)
37. F.T.Rettner, D.J.Auerbach and H.A.Michelsen *Phys.Rev.Lett.* **68**,1164 (1992)
38. H.A.Michelsen, C.T.Rettner, D.J.Auerbach and R.N.Zare *J.Chem.Phys.* **98**, 8294 (1993)
39. M.S.Dow and M.I.Baskes *Phys.Rev.* **B39**, 7441 (1983)
40. G.D.Billing *J.Phys.Chem* in press
41. G.D.Billing and M.Cacciatore *Chem.Phys.Lett.* **113**, 23 (1985)