Heterogeneous catalysis in interaction of plasma excited species with surfaces

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ABSTRACT

The interaction of excited species of a plasmas with surfaces may provoke heterogeneous catalytic effects. The specificity of these effects under non-equilibrium conditions are reviewed in this paper. The theoretical part is based on classical trajectories on LEPS potentials. The experimental parts presents a systematic collection of data from different fields.

RÉSUMÉ

L' interaction des espèces excitées du plasma avec la surface du matériau peut donner lieu à des phénomènes de catalyse hétérogène. La spécificité de ces phénomènes dans des conditions de non-equilibre est passée en revue. La partie théorique est basée sur le calcul des trajectoires sur des potentiels de type LEPS. La partie expérimentale est une collection des données des divers domaines du non-equilibre .

I. INTRODUCTION

Heterogeneous catalysis is a wide used practice in industry and a well developed chapter of chemical kinetics.

In the general theory of heterogeneous catalysis there is a tacit hypothesis: that in the gas surrounding the catalyst prevails thermodynamic equilibrium, as well as between the gas and the surface.

Number of interesting systems do not comply with this hypothesis, as for example upper atmosphere, plasma chemistry , laser chemistry etc. In these cases the gas phase is out of thermodynamic equilibrium, and molecules[1] posses intense internal excitation.

It is well known that the velocity of the reactions is very high when excited states of molecules are involved. Under these conditions the classical definition of catalysis as an increase of the rate of a reaction without change in the final amount of the products is no longer pertinent.

For the homogeneous gas phase non-equilibrium systems the dynamics of chemical reactions is well established both in theory and in experiment, essentially by use of molecular beams and lasers. In the heterogeneous systems the theory is in the very beginning and only scarce experimental results has been obtained.

The study of heterogeneous catalysis in non-equilibrium systems must answer three key questions:

a) is there any influence of the internal excitation on the rate of chemisorption?

b) do the products of the desorption have also non-equilibrium excitation?

c) how the (eventual) exothermic energy of the reaction is shared between the desorbing products and the solid ?

In the first part of this paper we describe briefly the stages of the heterogeneous catalytic processes. The theory will be summarised in the second part.

In the third part of this text an overview of experimental data meaningful for our subject is given. They come not only from heterogeneous catalysis but also from a wide variety of systems (etching, lasers etc.).

At the end an attempt is made to answer the three key questions mentioned beforehand in the case of plasmas.

II. THE FORMALISM OF HETEROGENEOUS CATALYSIS.

The are three main stages in heterogeneous catalysis:

II.1 Adsorption

The first step is the adsorption of the reactants on the surface:

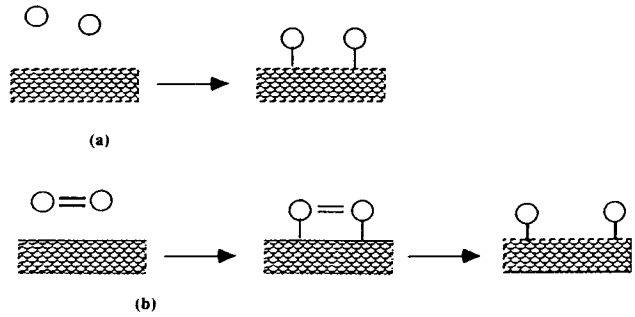


Fig 1. (a) adsorption (b) dissociative adsorption

The adsorption is not an spontaneous process. It depends on the interaction potential for the molecule-solid system.

More important for the chemist is the dissociative adsorption. In this case we "pay" the energy necessary to break the bond of the gas molecule $D_{A\text{-}B}$, but we "gain" the bond

energy of the two chemisorption bonds $\Delta H_{ads.}$ In total we spend much less energy to separate the reactant molecule(s) than in gas phase reactions.

II. 2 Surface Reaction and Desorption

These two stage are closely related. The adsorbed species migrate on the surface and react with other chemisorbed species (or with molecules from the gas phase)(Fig 2), The energy of the newly

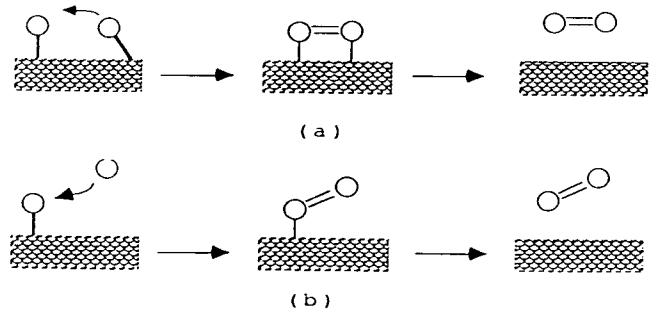


Fig.2 Surface Reaction (a) Langmuir- Hinshelwood mechanism (L-H)
(b) Eley-Rideal mechanism (E-R)

created chemical bond is partly used to break the chemisorption bond, and the excess of energy is shared between the solid surface and the molecule escaping to the gas phase. This sharing is defined by the accommodation coefficient γ. This is an important point for the non-equilibrium excitation of the reaction products.

III. NON EQUILIBRIUM REACTION DYNAMICS.

The main particularity of chemical reactions in plasmas is due to the high internal excitation of the molecules, in most cases under non-equilibrium distributions. From the point of view of the chemist, this is reflected to the variation of the cross section of a reaction path[2], when the energy is channelled preferentially to some degrees of freedom of the molecules[3]

To this day, the theoretical treatment of heterogeneous reaction systems in non-equilibrium conditions is workable only as a modification of the dynamics of chemical reactions in the gas phase . For this reason we will first recall the main features of the gas phase systems, focusing our interest to the influence on the reaction rate of the non-equilibrium excitation of the plasma molecules

III.1 Gas phase systems.

The reaction takes place along the minimum energy path of the Potential Energy Surface (PES) of the interacting atoms involved. The most useful PES are the semi-empirical LEPS potentials. For a three atom reaction of the type

$$A + BC \longrightarrow AB + C$$

the PES can be described in terms of the interatomic distances r_{ab} and r_{bc}

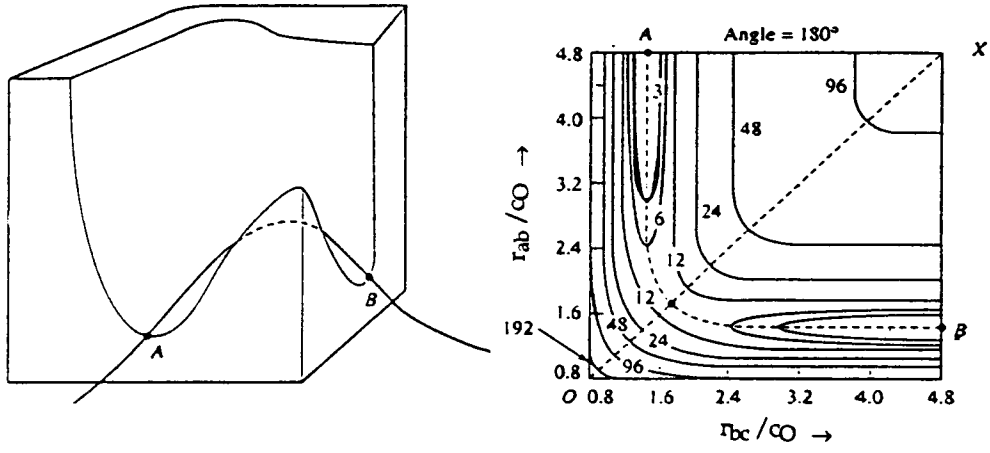


Fig.3 PES and energy barriers in the gas phase.

Depending on the position of the energy barrier (in the entry or the exit valley of the PES), the influence of the non-equilibrium of the reactants has a different role (for a given amount of total energy):

-if the barrier is the entry valley (usual in exo-thermic reactions) the translational excitation of the reactants increase the cross section of the reaction (fig.4a). The products carry the excess energy mainly as vibrational excitation.

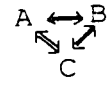
-if the energy barrier is in the exit valley (characteristic of endo-thermic reactions) the cross section will increase with an preferential excitation of the vibrational degrees of freedom of the reactants (fig.4b).

III.2 Heterogeneous catalysis.

The direct theoretical treatment of state-resolved reactive molecule-surface interaction is an overwhelming theoretical problem. This is due to numerous causes: the lack of precise infraction potential, the creation of various, not easy to formalise, kinds of bonds, the existence of precursor states, of energy transfer by inelastic collisions prior to the adsorption, of electron-hole pair and phonon interactions, etc.

An effort of quantum mechanical treatment has be made by Baer[4]. But systematic studies with more practical interest was made by Wolken and his co-workers.[5] which used LEPS potentials and classical trajectories. LEPS potentials give only qualitative picture of the reactive PES, which nevertheless allow classical trajectories calculations.

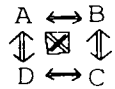
Usually the PES of the three-atom system in the gas phase:



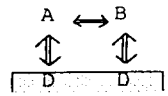
is represented by considering the pairwise interactions U_{ij}:

$$U_{IJ} = \frac{Q_{IJ} + J_{IJ}}{1 + S_{IJ}^2} = D_{IJ}\left[\exp\left(-2\alpha_{ij}\left(r_{ij} - r_{ijo}\right)\right) - 2\exp\left(-\alpha_{ij}\left(r_{ij} - r_{ij0}\right)\right)\right]$$

D_{ij}= Bond energy Q_{ij}= Coulomb integral S^2_{ij}= Overlap integral J_{ij} = Exchange integral α_{ij} = Morse parameter r_{ij}= distance between atoms i and j r_{ij0}= distance in equilibrium.
In the case of a four atoms system in the gas phase the interactions can not be limited to pairwise potentials:



But in the heterogeneous systems when D and C are atoms of the solid the interaction is simplified, because (in a first approximation) the solid can offer equivalent electrons in any point of the surface :



In this case the pairwise interactions can be maintained. The interaction potential U_{ABCD} is given by:

$$U_{ABCD} = \frac{1}{1+\Delta}\left[u_{AB} + u_{AD} + u_{BC} - \left[\ A_{AB}^2 + \left(A_{AD} + A_{BC}\right)^2 - A_{AB}\left(A_{AD} + A_{BC}\right)\ \right]^{1/2}\right]$$

where

$$u_{ij} = \frac{D_{ij}}{4}\left[\left(3+\Delta\right)\exp\left(-2a_{ij}\left(r_{ij} - r_{ij_0}\right)\right) - \left(2+6\Delta\right)\exp\left(-a_{ij}\left(r_{ij} - r_{ij_0}\right)\right)\right]$$

$$A_{ij} = \frac{D_{ij}}{4}\left[\left(1+3\Delta\right)\exp\exp\left(-2a_{ij}\left(r_{ij} - r_{ij_0}\right)\right) - \left(6+2\Delta\right)\exp\left(-a_{ij}\left(r_{ij} - r_{ij_0}\right)\right)\right]$$

$$\Delta = S^2 = S^2_{AB} = S^2_{AD} = S^2_{BC}$$

The corresponding PES does not have significant qualitative differences from the corresponding PES for homogeneous gas phase systems. But very few case have been studied until now, because realistic particle-surface potentials are complex, even in the simplest systems.

III.2.1 Adsorption Potentials.

The main parameter in this stage is the adsorption probability (or sticking coefficient) of the reactants on the surface.

There are three possible situations, depending on the existence of energy barrier for the adsorption . They are illustrated in the fig.4 in the case of adsorption of H_2 on W[4] .

The location of the saddle point (barrier on the minimum energy path) is sensible to the plane of the crystal and to the relative position of the addatom vis-a-vis to the atoms of the solid (atop to one or bridge between two or four atoms). This is illustrated in fig 5 for the system H2-Ni (after[15]):

a) No energy barrier to the adsorption.

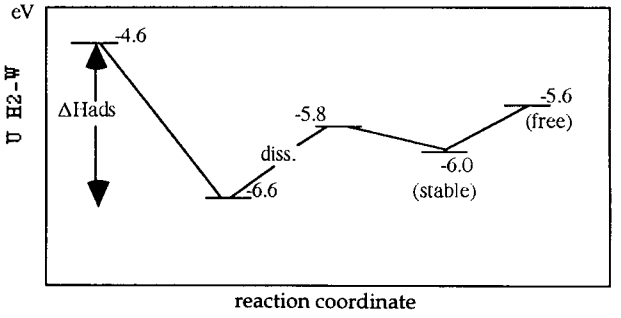


Fig. 4a. Energetics of the adsorption of Hydrogen on tungsten without energy barrier.

b)Small energy barrier.

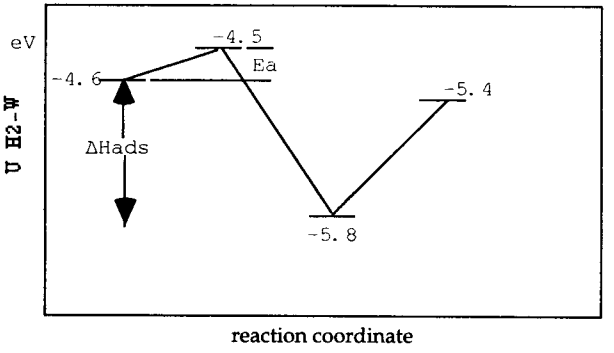


Fig. 4b. Energetics of the adsorption of Hydrogen on tungsten with Ea=0.06eV energy barrier.

c)Important energy barrier

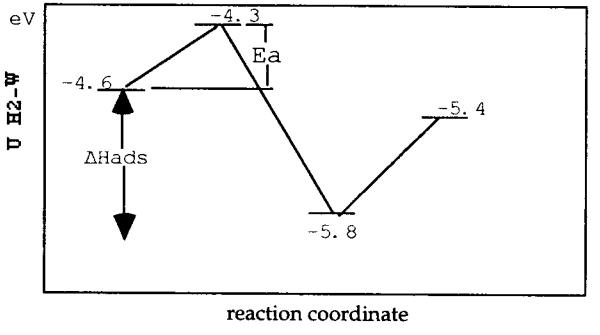


Fig. 4c. Energetics of the adsorption of Hydrogen on tungsten with Ea=0.15eV energy barrier.

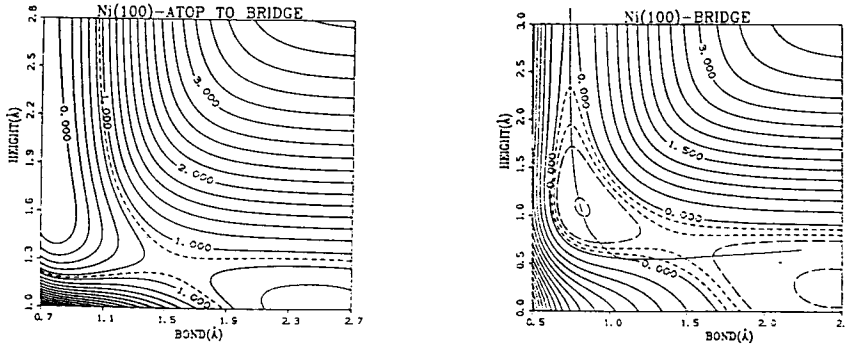


Fig. 5a PES of dissociation of H_2 on Ni (100) plane, corresponding to two different adatom positions. The right PES has not barrier. (Energy values refer to free H_2 molecule).

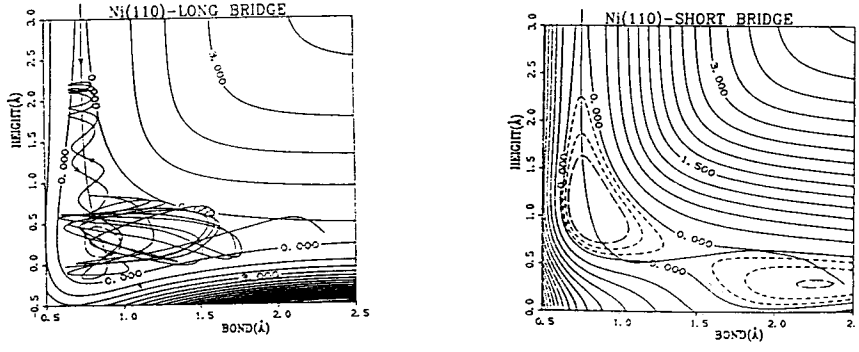


Fig. 5b: PES of dissociation of H_2 on Ni (110) plane.

Some general conclusions can be drown from these simulations:

- the key parameter is the translational energy. There is a threshold for this energy (the energy barrier or activation energy) beyond which the effect of internal excitation is manifest.

- from the chemical point of view, particular interest has the dissociative adsorption. The simulation shows that the vibrational excitation of the reactants enhances the probability of dissociative adsorption.

In table 1 we present the results of the simulation of the dissociative adsorption of H_2 on Ni made by Lee and DePristo[15], using classical trajectories on LEPS potentials.

Initial (n,j)	E_{kin} (eV)	Sticking probability		
		Ni(100)	Ni(110)	Ni(111)
(0,0)	0,03	0,37	0,55	0,01
"	0.05	0,28	0,58	0,01
"	0,06	...	...	0,02
"	0,07	0,30	0,59	0,06
"	0,10	0,32	0,58	0,06
"	0,14	0,28	0,58	0,08
"	0,20	0,32	0,59	0,08
(1,0)	0,05	0,38	0,59	0,28
"	0,10	0,33	0,64	0,32
"	0,20	0,50	0,63	0,37
(0,5)	0,10	0,32	0,62	0,15

Table 1. Sticking probabilities of H_2on different surfaces of Ni as a function of vibrational (n) and rotational (j) states of H_2, for different values of kinetic energy

A strong influence of vibrational excitation is observed except for surface (110) when this influence is less pronounced. It is important to point out that in the PES of (110) surface there is no energy barrier.

III.2.2. Energetics of Desorption.

As we pointed out the reaction-desorption process is exoergic. Two questions are pertinent concerning the desorbing reaction products:

- Which part of the excess energy do they carry?

- Do they have non-equilibrium excitation?

The simulation is made on the same PES for the N_2-W system we show in the preceding paragraph. For the excitation of the reactants the results are shown in fig. 6. It is obvious that for attractive PES the desorption probabolity is very low.

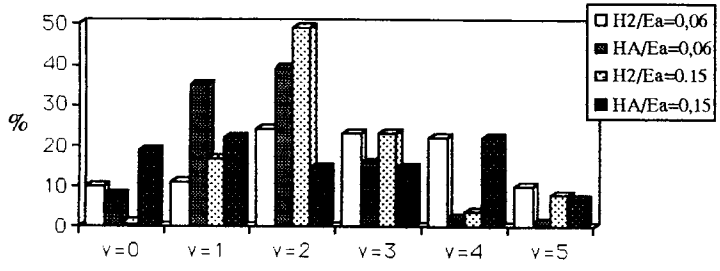


Fig 6 Population of vibrational levels of the products
HA is a combination of an H atom with a heavier atom

For repulsive PES with energy barrier the simulation shows that the desorbing molecules have non-equilibrium excitation under certain conditions.(Fig 6). The populations of vibrational levels of the products are bell-shaped, but discrepacies from the Boltzmann distribution are important.

The sharing of the energy carried by the molecule is shown in fig. 7:

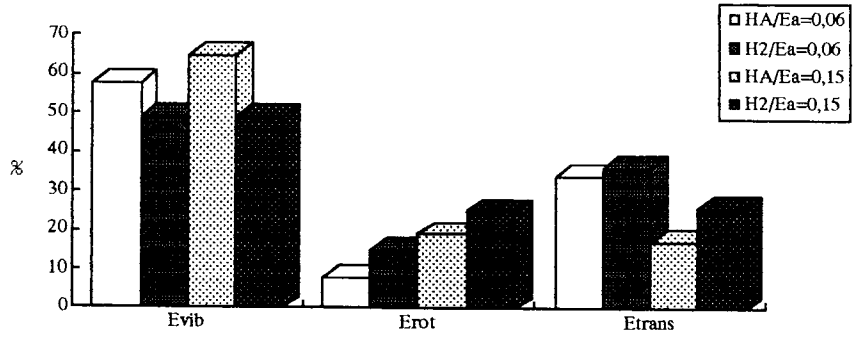


Fig 7 Energy distribution in products

A non-equilibrium excitation of the products arise from the simulation, the main part being channelled to the vibration of the molecules. This point is important, because it predicts that the presence of catalytic surfaces in plasma reactors will maintain and probably increase the non-equilibrium character of the discharge. The creation of chemical lasers by heterogeneous catalytic reaction has been presumed in the basis of these results.

Tully[5] has conducted similar simulation for the oxidation of C atoms adsorbed on Pt by gas phase O (Eley-Rideal mechanism). The reaction is strongly exothermic. The product CO molecule carry the most part of this energy. The distribution of the excitation in CO is shown in fig. 8.

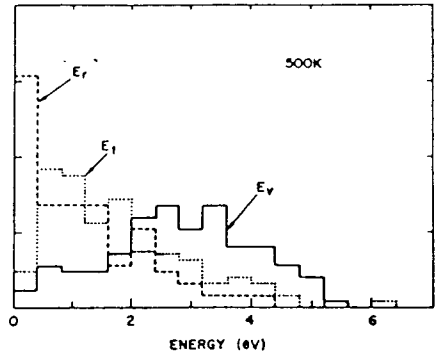


Fig. 8 Energy distribution of desorbing CO molecules.

III.2.3. Energy partitioning in the desorption.

The simulation shows a non equal partitioning of the energy between the catalyst and the gas Fig.9. The general rule is that the gas molecule takes the main part of the energy. This is an important point, as it corresponds to an enhancement of the non-equilibrium of the plasma. From a practical point of view it suggests the possibility of "cooling" a solid object in contact with partly ionised gazes (plasmas, upper atmosphere etc.).

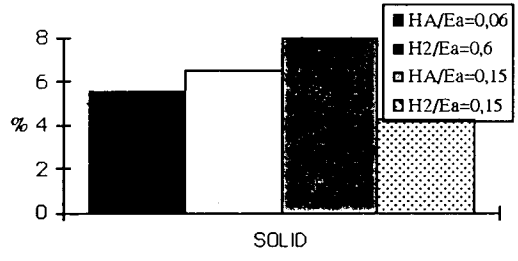


Fig 9. Percentage of the excess energy carried by the catalyst

IV. EXPERIMENTAL DATA

Very few systematic detailed experimental studies has been made in plasmas[7,8] Most of the useful data found in the bibliography comes from less complex experimental techniques, as molecular beams and lasers. Nevertheless these results are useful for plasma chemistry,

because the different processes involved in heterogeneous catalysis are examined separately and with satisfactory precision.

In a systematic study of non-equilibrium in catalysis in plasmas we studied the distribution of the internal excitation of N_2 desorbing from different surfaces after decomposition of NH_3[9,8] The non-equilibrium of the plasma was greatly enhanced by the catalytic reaction. This is obvious from fig.10a. With surfaces without catalytic properties this enhancement was switched to thermalisation (Fig. 10b)

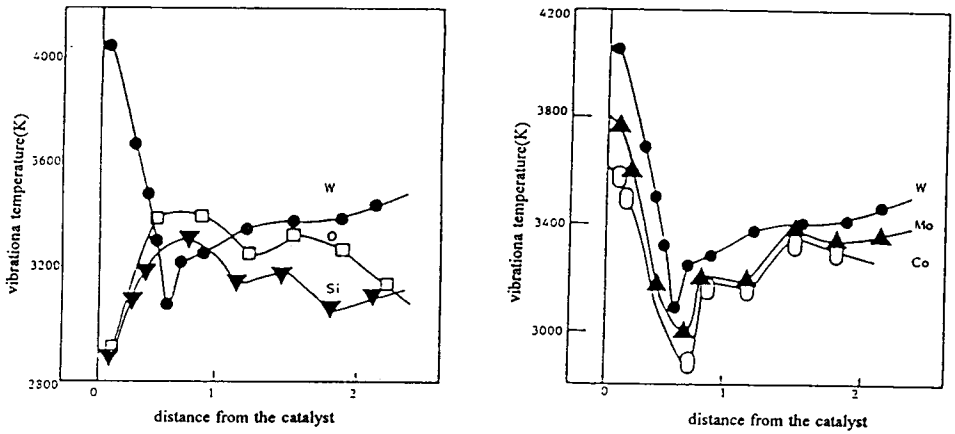


Fig.10 a: Vibrational temperature of desorbing N_2 for different catalysts. b: Comparison of a catalyst(W), of a non catalyst (Si) and of the plasma without any surface.

The experiments performed directly in a plasma reactor do not allow to obtain state-resolved analysis of the excitation of the reaction products. Simpler systems, essentially molecules beams, was used to achieve this goal.

IV.1 Adsorption.

We present the influence of different excitation modes of the reactants to the adsorption probability.

IV.1.1. Vibrational excitation.

The great majority of experiments show an enhancement of the sticking probability with the vibrational excitation of the impinging molecules.

Kubiak et all.[10] studied the chemisorption of H_2 on Cu. By measurement of the distribution of the desorption products and by application of the microscopic reversibility principle, they concluded that a great enhancement of the sticking coefficient would come from vibrationnally excited molecules.

Gadjuk and Norkov [11] studied different systems. In their studies molecules having important translational energy acquire vibrational excitation by collision with the surface. This vibrational excitation was found to increase the sticking coefficient.

In experiments in laser induced gas-surface interactions Chuang[12] studied the vibrational excitation of SF_6 with CO_2 laser allowed the SF_6 to react chemically with the otherwise inert Si surface.

Bass et al.[13] found that the decomposition of N_2O on Cu surface was enhanced by factor 10^3 when N_2O molecules was vibrationally excited by a N_2O IR laser.

Umstead and Lin[14] studied a more complex molecule, by using the dissociation of HCOOH catalysed by Pt. The comparison of decomposition rate in presence and in absence of vibrational excitation of HCOOH by a CO_2 laser showed an important enhancement of the decomposition when the laser was turned on.

The activation of CH_4 chemisorption by vibrational excitation appears more controversial. From the study of Steward et al.[15] of isotope and kinetic effects on CH_4 dissociative chemisorption on Rh, vibrational excitation seems to be the main channel for this process. Winters[16] arrived to similar conclusions in the study of CH_4 dissociation on W.

In a more exhaustive study of CH_4 dissociative chemisorption on W Rettner at al.[17] shown that vibrational excitation enhances the chemisorption probability, but this enlargement is not, in average, significantly larger than for equivalent amount of energy placed into translation.

The conclusion of Brass et al.[18] was analogous. The excitation of the ν_3 and $2\nu_3$ vibrational modes using either He-Ne laser or arc sources did not produced any detectable change on the rate of chemisorption of CH_4 on Rh films.

Similar experiments where carried out in the BCl_3- stainless steel system by Gochelashvili et al[19] . They conclude that the excitation of ν_3 vibrational mode of BCl_3 by CO_2 laser decreased the sticking coefficient.

None of these experimental studies contain a straightforward proof concerning the effect on adsorption of the activation of a specific vibration of the impinging molecule. Nevertheless they give strong evidence that this effect is positive in general. Only the knowledge of PES and the energy barriers would give satisfactory explanation of the exemptions to this rule.

IV.1.2. Rotation.

State-resolved experiments with preferential rotational excitation of the reactants are difficult to realise, because of the rapid relaxation to translational modes. Only indirect experimental conclusions and calculations has been made. The general conclusion is the absence of important influence of rotation in adsorption.

In the H_2 dissociative chemisorption on Ni, Lee and De Pristo[20] observed a significant role of rotational excitation only on adsorption on Ni(111) surface. For Ni(100) and Ni(110) surfaces the rotational excitation does not change the dissociation probability.

Analogous small influence of rotation was observed by Kubiak et all.(5) for the chemisorption of H_2 on Cu.

According to the quantum mechanical approach of Baer(3), for a given initially rotating molecule the chemisorption is possible only if the axis of rotation is parallel to the surface. This probably explains the above differences according to the plane of the crystal.

IV.1.3.Translation.

Generally, increasing the translational energy enhances the sticking probability.

Hamza and Madix[21] observed the dissociative adsorption of H_2 on Ni(100) in molecular beam experiments. There is an activation barrier to the adsorption ant they found that the adsorption is translationally activated.

The plane of Ni plays an important role. Steinruck et al.[22] investigated an increase of the sticking coefficient of H_2 on the (111) surface, a slight decrease on (110) and no effect on (100) surface.

These results has to be compared with the simulation of Lee and DePristo[15], who predicted for the same system no effect on (110) and (100) surfaces and strong dependence for the (111) surface of Ni.

For the chemisorption of N_2 on W, it was found in molecular beam experiments an increase by a factor 10^2 of the sticking probability for 1eV increase in translational energy[12,23]. Even more impressive increase was reported for the dissociative adsorption of CH_4 on W, of the order of 10^5.

The opposite situation appears in the associative adsorption of CO on Ni(111)[24] where the sticking coefficient at zero coverage was found to decrease with incident translational energy.

The adsorption of H_2 on Cu surfaces was studies in nozzle beam experiments[25]. The adsorption has an activation barrier and five times increase of adsorption probability was observed with the increase of translational energy.

IV.2. Desorption.

There is a general agreement that a non-equilibrium distribution of excitation on the products of the catalytic reaction arise when they desorb from the surface.

IV.2.1. Vibration.

The desorbing molecules posses high vibrational excitation. In a pioneer work, Bernacek[26] observed the vibrational temperature of the desorbing N_2 from poly-Fe to be significantly higher than the temperature of iron surface.

The vibrational excitation of CO_2 molecules produced by oxidation of CO on platinum surface was also found to exceed the temperature of the solid T_s[27 28].

Kori and Halpern[29] in IR emission spectroscopy studies observed very high vibrational excitation, up to v=7, of CO desorbing from poly-Pt after oxidation of adsorbed C by oxygen. The population followed statistical distribution.

Comparable results was obtained by the same authors on the oxidation of adsorbed CO by O atoms on Pt[30]. They obtained high vibrational excitation of CO_2 and observed non-statistical, inverted vibrational distribution.

The rate of the vibrational populations (v"=1/v"=0) was measured in the H_2 desorbing from Cu[5]. They found it to be 0,052, significantly greater than the value 0,0009 which correspond to equilibrium with surface temperature.

IV.2.2.Rotation.

The rotational excitation of the products is lower than that expected from equilibrium with the surface.

Cavanagh observed by laser induced fluorescence the rotational energy of NO desorbing from Ru(001) surface[31]. They found Boltzmann distribution for the rotation $T_{rot}=235 \pm 35$ K, compared to the surface temperature of $T_s = 455 \pm 20$ K.

Similar results was obtained by Bernasek[27,28] whithN_2 molecules desorbing from sulphur contaminated Fe. The rotational temperature of N_2 was 400±30 K, compared with more then a thousand degrees for the surface temperature.

Rotational energies lower than the surface temperature was also found by Muhlhausen et al[32] in a study of the dynamics of non-reactive scattering and desorption of NO from Ag and Pt surfaces.

Zacharias [33] observed by laser induced fluorescence the rotational states distribution of H_2 desorbing from poly-Pd. Non-Boltzmann populations was detected and the average rotational energy was less than the surface temperature.

LIF was also used by Talley[34] to observe the rotational temperature of OH radicals desorbing after the oxidation of hydrogen on poly-Pt. In this study the rotational temperature was found to be in thermal equilibrium with surface temperature.

IV.2.3. Translation

Not only the internal energy of desorbing molecules, but also the translational energy can be different from the surface temperature.

Lin and Somorjai[35] in molecular beam experiments found that the translational energy of HD molecules desorbing from Pt stepped surface is lower than the temperature of the surface.

The translational energy of CO_2 desorbing from Pt(111) surface after catalytic oxidation of CO has been found to be in excess. Becker et al[36] measured translational energy up to 3560 K for a surface temperature of 880 K.

On the contrary translational temperatures lower than that of the surface was predicted by Muhlhausen et al[32] in the case of NO desorption from Ag and Pt.

Talley[34] observed almost equal surface and translational temperatures in OH radicals desorbing from poly-Pt.

V. CONCLUSION

The non-equilibrium character of internal excitation of plasma species seems to play an important role in the heterogeneous catalysis. Both dynamics simulations and experiment show than in adsorption the non-equilibrium excitation of the reactants influences the adsorption probability.

A minimum of kinetic energy is first of all necessary in order to achieve this step. A key parameter is also the energy barrier for this step. Vibrational excitation seems the more efficient in order to overcome this barrier.

The desorption of the reaction products also creates non-equilibrium. It is reasonable to admit that, before the desorption, the adatoms are in thermal equilibrium with the surface. When ejected back to the gas phase, the products often exhibit high internal excitation and even kinetic energy.

These conclusions are simply general tendencies. For every system the calculation of PES would only give a satisfactory scientific background to the elucidation of the role of internal excitation.

In plasma chemistry these general tendencies are very useful to have in mind in order to interpret the experimental results . This is because almost all the possible excitation modes coexist in plasma reactors and state-resolved experimental data impossible to obtain.

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[2]for a given total energy

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