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SPRING COLLEGE IN CONDENSED MATTER
ON
"THE INTERACTION OF ATOMS & MOLECULES WITH SOLID SURFACES"
(25 April - 17 June 1988)

THE KINETICS AND DYNAMICS OF GAS-SURFACE PROCESSES
(Lecture II)

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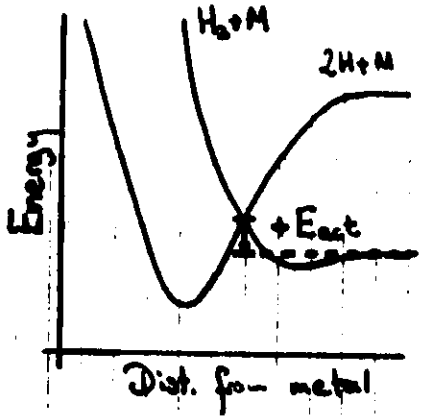
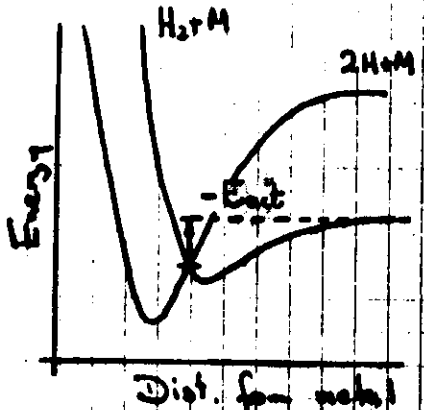
H_2 - Metal Interaction

Pre-history (pre 1960)

Experimental studies on powders.
Adsorption rates measured on Ni, Cu ....

Lennard Jones model



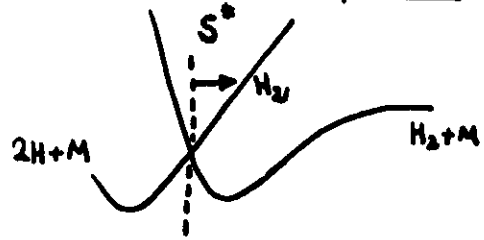


"Activated desorption" "Non-activated"

Assuming TST to hold, what would the products look like for each of these cases?

Comsa + David, Surf. Sci. Rpt. 5 (1985)

(i) Non-activated desorption



Molecules leave surface with equilibrium distribution at T_s,

$$p(v)dv \sim v^3 \cos\theta\, e^{-\beta v^2/2M}\, dv$$

# of molecules / sec / unit solid Δ between v, $v+dv$

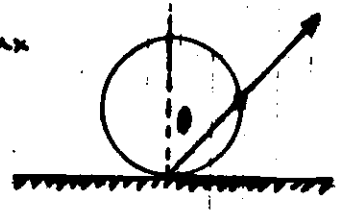
Angular dist^n of emitted flux

$$N(\theta) \sim \cos\theta \quad \text{[Knudsen Law]}$$

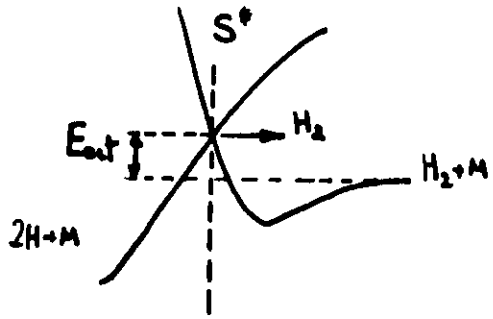
Mean energy of emitted flux in θ

$$\ll E(\theta) \gg = 2kT_s$$

Desorbing flux "$\cos\theta$"



(ii) Activated desorption



If $\frac{1}{2}Mv^{*2} = E_{act}$ then,

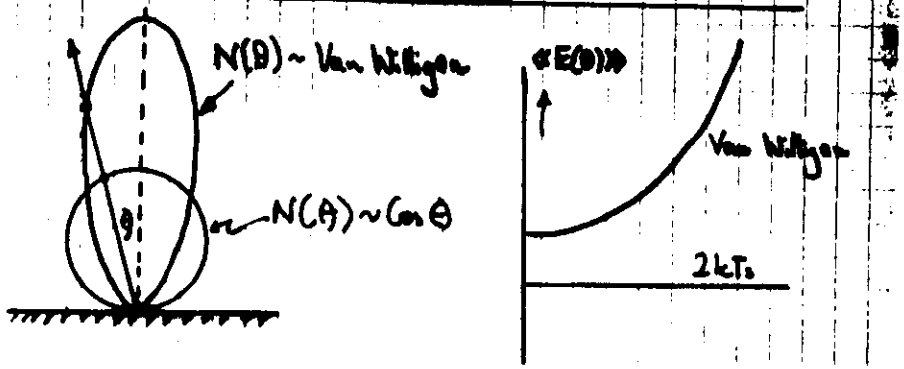
$$P(v)dv \sim v^3 \cos\theta\, e^{-\beta\left(\frac{1}{2}Mv^2 - E_{act}\right)}\,\Theta\left[v\cos\theta - v^*\right]\,dv$$

Angular distⁿ

$$N(\theta) \sim \left\{\frac{E_{act} + kT_s\cos^2\theta}{(E_{act}+kT_s)\cos\theta}\right\} e^{-\left\{\left[E_{act}/kT_s\right]\tan^2\theta\right\}}$$

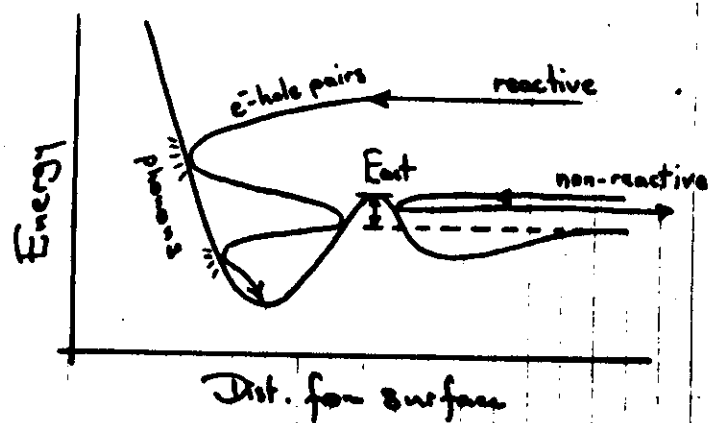
Mean energy

$$\ll E(\theta)\gg = 2kT_s\left[1 + \frac{1}{2}\left\{\frac{E_{act}^2}{(E_{act}+kT_s\cos^2\theta)kT_s\cos^2\theta}\right\}\right]$$



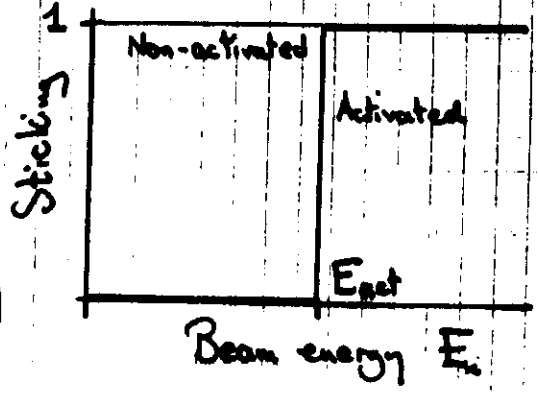
Adsorption

Let us suppose that energy transfer to the solid is super-efficient ($\sigma = 1$) "like a golf ball into a sand-trap"



In order to surmount the barrier the beam translational energy

$E_i > E_{act}$



[Tom Grimley]

Experimental work

Pre-history (0 → 1960)

Adsorption on powders and films.
Irreproducible results.

H_2 / Cu - $0.1eV \leq E_{act} \leq 1.5eV$
H_2 / Ni - $E_{act} \sim 0eV$ or small !!

History (1960-1970)

Hydrogen found to dissociatively adsorb on Cu and Ni surfaces ($\Delta\varphi$).

Cu - $E_{act} \sim 0.5eV$
Ni - $E_{act} \sim 0.1eV$

Experiments on evaporated films.

Pre-modern (1970-1980)

H_2 permeation technique exploited to study desorption

High flux of H_2 at detector

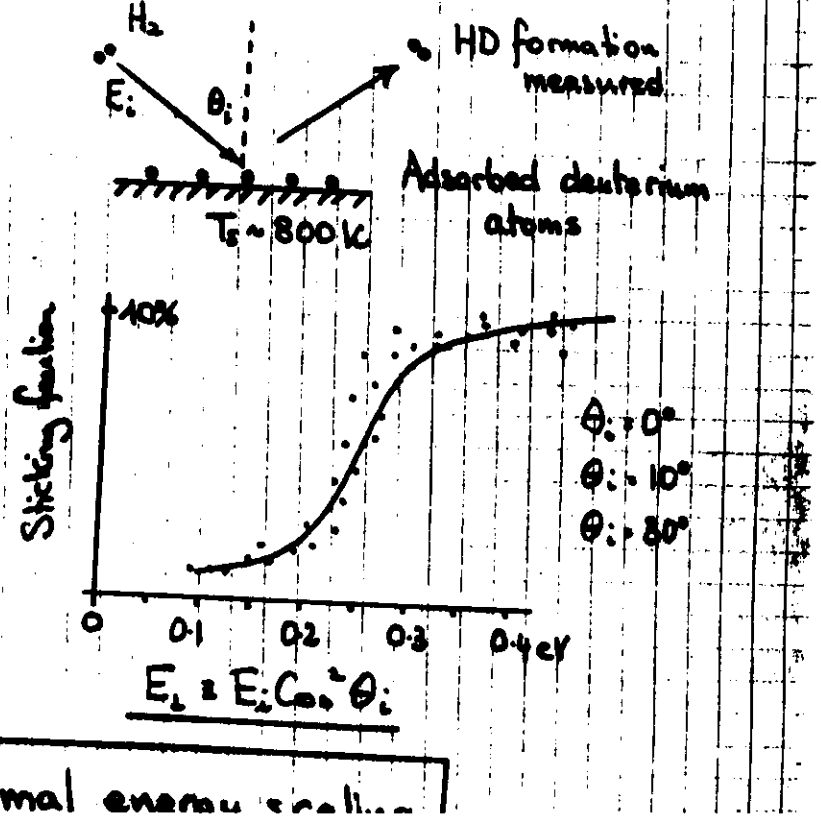
Balooch + Stickney H_2/Cu

$N(\theta) \sim \cos^n\theta$ ← no obvious reason for this

- ⇒ Cu(100) $n = 5$ $E_{act} = 0.25eV$
- ⇒ Cu(110) $n = 2.5$ $0.1eV$
- ⇒ Cu(111) $n = 6$ $0.25eV$

} 1-D barrier

Balooch, Cardillo, Miller + Stickney

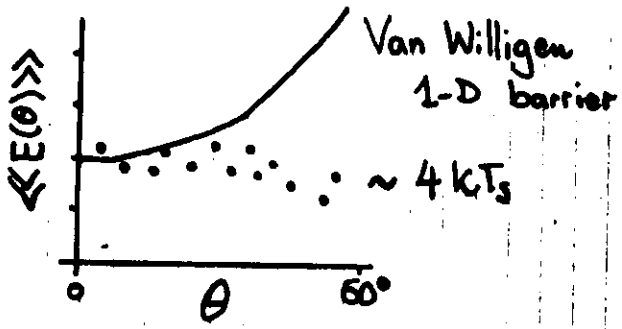


Normal energy scaling

Modern (1980 - present)

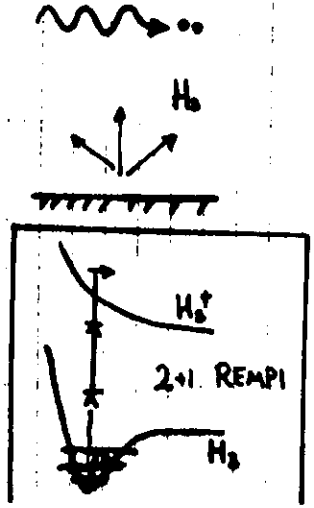
Comsa + David

Permeation experiment to measure the velocity distribution of desorbing species $f_n(\theta)$.



Kubiak, Sitz + Zare

two (193–211nm)



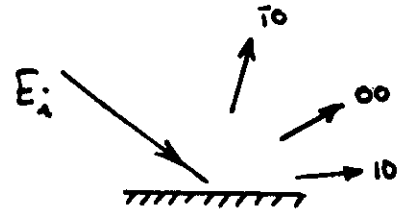
Permeation of H_2 + D_2 through Cu(110) - (111).
Measurement of vibrational and rotational distributions

Vibrations: $P_{v=1}/P_{v=0} \sim 90 \times$ Boltz

Rotations: Non Boltzmann
$\langle E_{rot} \rangle < kT_s$

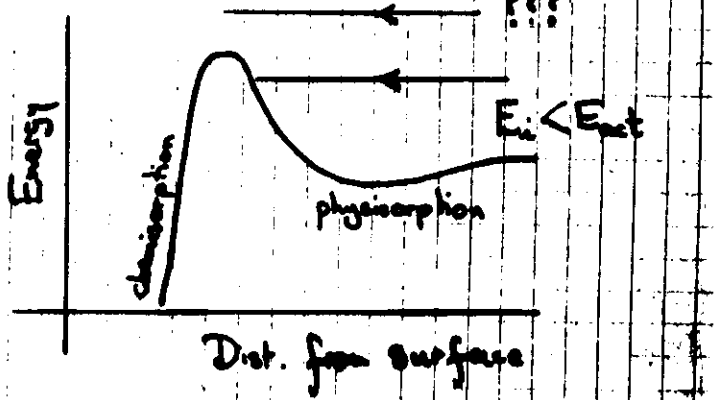
Lapujoulade + Perreau

Diffraction of H_2 and D_2 beams from Cu(110) surface.



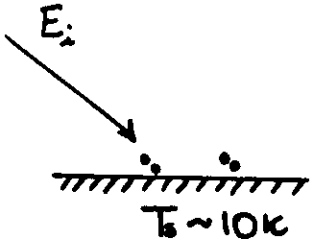
Attempting to find E_{act}, scan of diffraction with E_i:

Nothing dramatic at 0.25eV!!



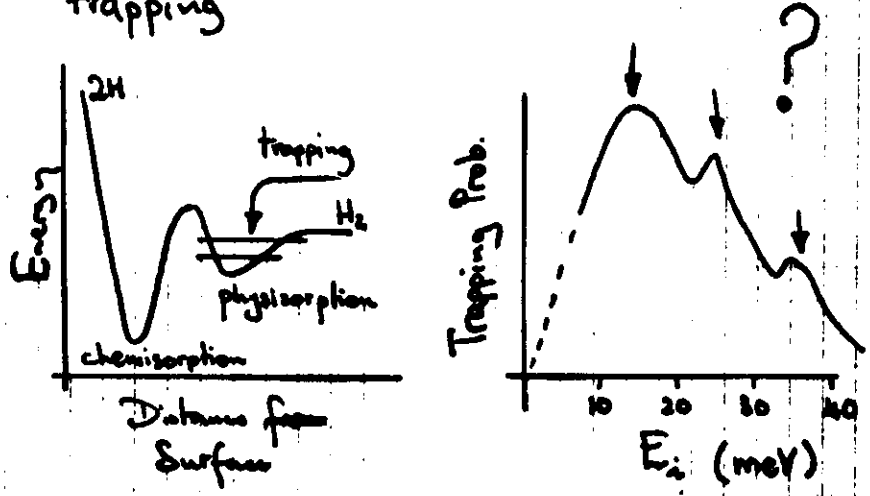
What is the nature of the barrier?

Andersson, Wilzén + Harris



Molecular trapping.

In a scattering experiment, interesting resonances were observed in H_2 trapping



They argued that these were not bound states of the static potential but many-body resonances.

(wip)

H_2/Ni

(111): Robota et al, Rendulic et al, Hayward + Taylor.

> $15 \leq E_{act} \leq 100$ meV
> 'Normal' scaling of sticking not observed.
> Strong diffraction observed at all energies.

(110): Robota et al, Rendulic et al, Hamza + Madix.

> $E_{act} = 0$! (or $E_{act} > 34$ meV)
> Diffraction observed
> $S_0 \sim 1$ (or $0.2 \leq S_0 \leq 0.5$)

(100): Rendulic et al, Hamza + Madix

> $0.1 \leq S_0 \leq 0.2$
> Significant isotope effect
> $S_0(H_2) > S_0(D_2)$ (opposite to results of Balooch et al on Cu)

Theoretical Models for H_2/Metal Potential Energy Surfaces.

(i) Semi-infinite [Je-based]

$H_2/Mg(001)$.

> True, delocalised states on surface.

> Exchange-correlation - LD: DFT

> Substrate atoms included perturbatively

(ii) Cluster calculation

H_2/Cu & H_2/Ni

> "Surface" treated as a cluster of 2 atoms.

> Exchange-correlation - LD: DFT

> Substrate + adsorbate species treated on equal footing.

ground. Lattice effects, ΔE_H^L, are then accounted for by treating the difference ΔV between the pseudopotentials from the ion cores and the potential from the positive background in first-order perturbation theory.[5,6] The energy of a hydrogen atom at a position $\vec{r}$ outside the surface is thus calculated as $E_H(\vec{r}) = E_H^{jel}(z) + \Delta E_H^L(\vec{r})$,[5] where z is the distance from the surface. The weakness of the pseudopotentials makes this a reasonable procedure.[5,6]

The energy $E_{H_2}(\vec{r}, \vec{R})$ of an H_2 molecule centered at the position $\vec{r}$ outside the surface and with the nuclei at $\vec{r} \pm \frac{1}{2}\vec{R}$ naturally splits into two parts,[6,9]

$$E_{H_2}(\vec{r}, \vec{R}) = E_{extra}(\vec{r}, \vec{R}) + E_{intra}(z, R), \qquad (1)$$

energy E_{intra} to be approximated by the value in the jellium model at each distance z from the surface and at each internuclear separation R. In the jellium model, E_{intra} has been calculated self-consistently for H_2 perpendicular[9] and parallel[9] to the surface. The accuracy obtained with these approximations, amounting to some tenths of an electron volt in total energies and to smaller values for energy differences, is sufficient to identify some of the concepts of adsorption kinetics and to give them an interpretation in terms of the electron structure of the adsorbate-substrate system. "Chemical accuracy" [$\sim kT \sim 0.025$ eV at room temperature] is not obtained, however.

The initial increase in energy seen in Fig. 1,

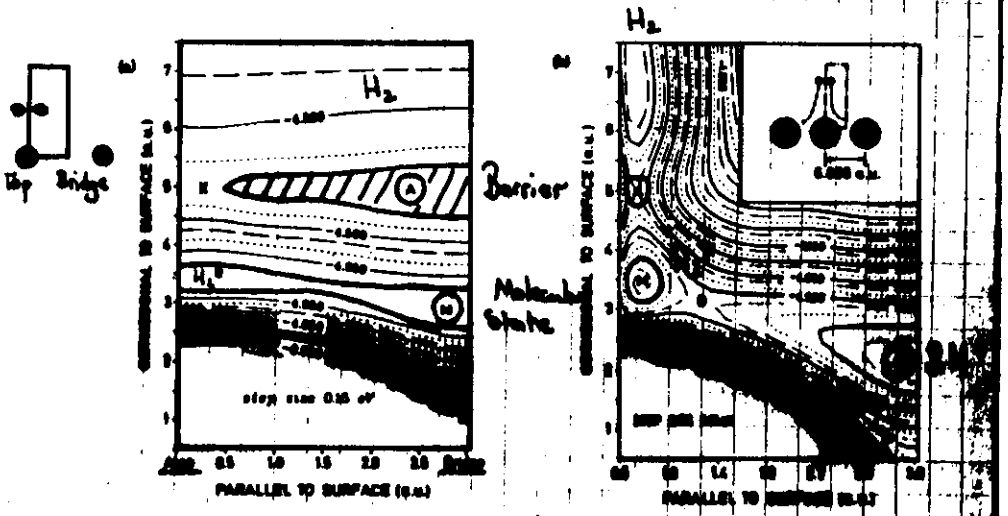


FIG. 1. Equipotential-energy curves for H_2 on a Mg(001) surface, (a) with H_2 parallel to the surface and a bond length of $R = 1.2$ a.u., and (b) descending over the atop site and the bridge site from perpendicular to parallel. The energies in electron volts are relative to those of the free [illegible]. The molecular dissociation energy in (a) is found only 0.1 eV relative to a free molecule. The distance from the surface is measured from the first atomic layer, and the distance parallel to the surface, which is (a) equal and half the H-H separation R, is measured from the atop site towards the bridge site. The coordinates of (a) gives the minimum between the two points. This saddle point is the one that has represented the activation barrier A against [illegible] dissociation [illegible] to the surface into the H-H vibration parallel to the surface. Therefore, the molecule will [illegible] easily, even though the dissociation barrier D is of the same size as A.

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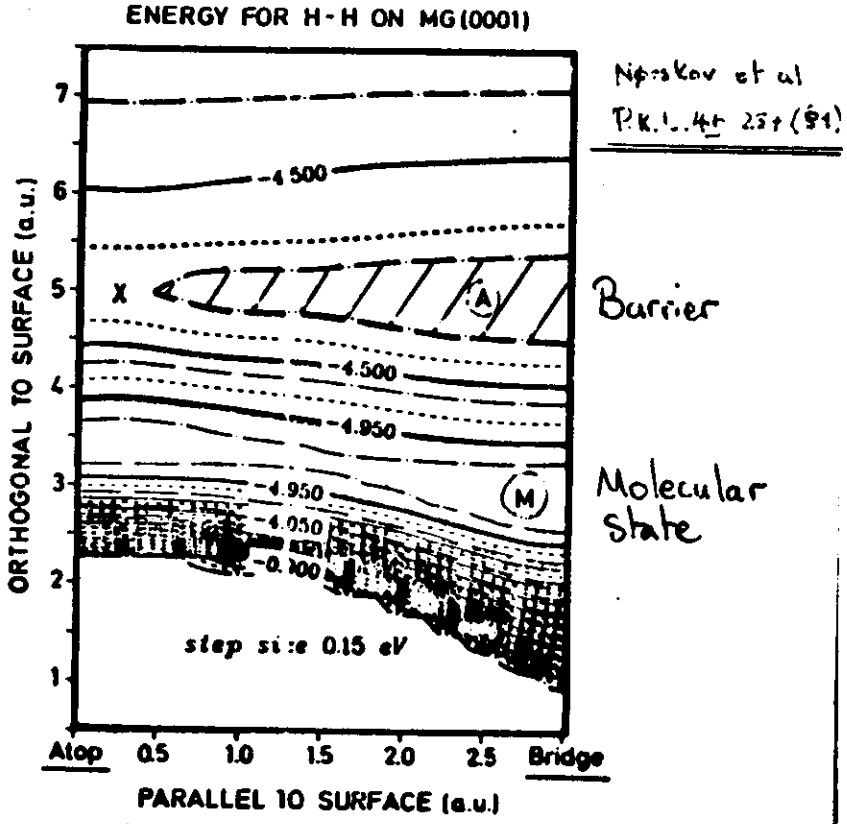
Norskov et al
PRL 46 (1981) 257

$H_2/Mg(001)$

[c.f. Bengt Lundqvist]

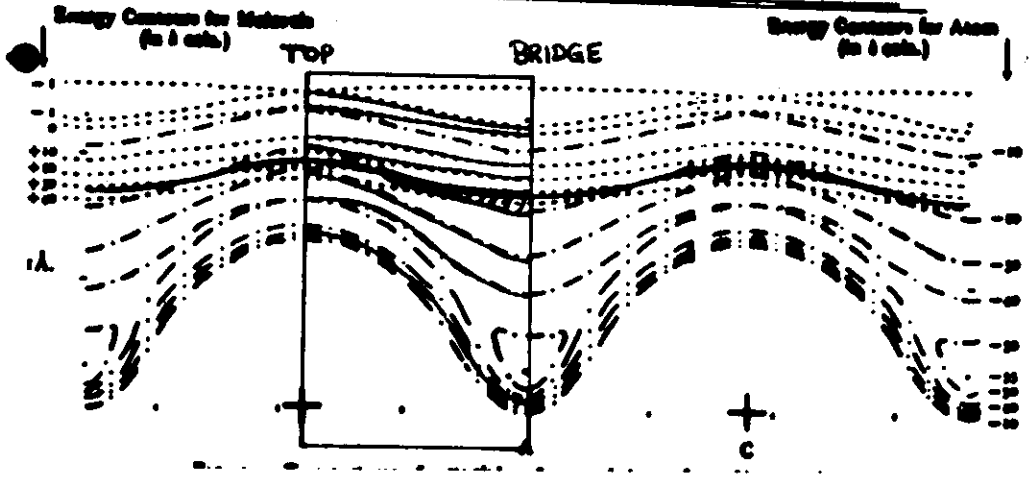


Nikitskov et al
T.F.S. 44 257 ('61)

Barrier

Molecular state

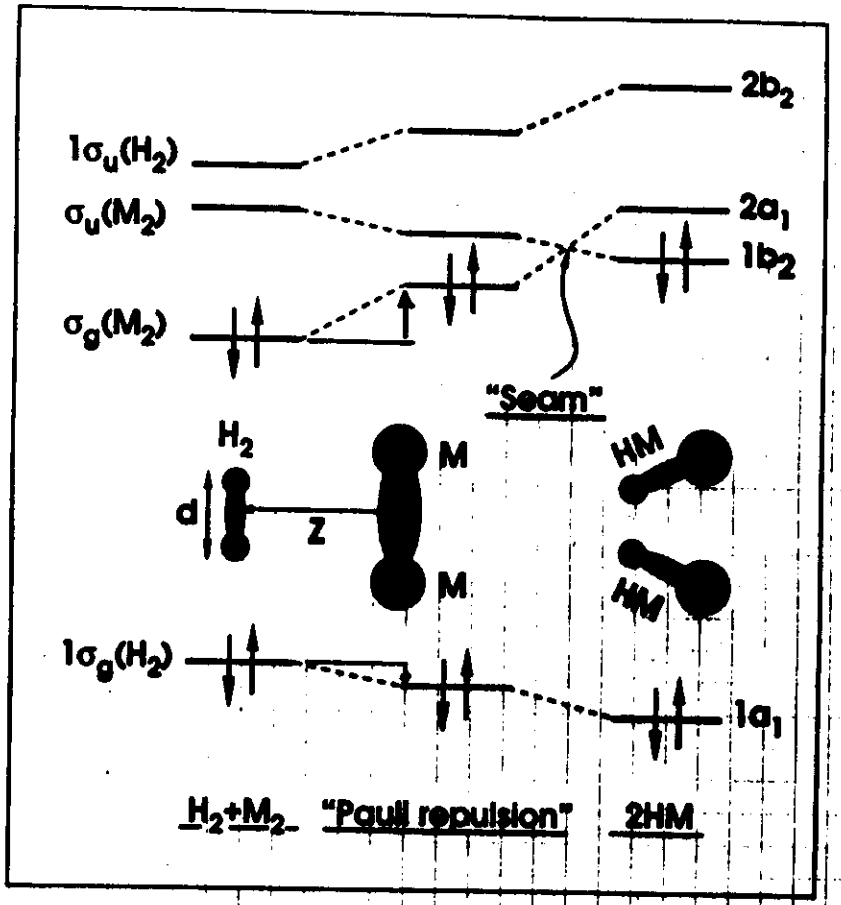
Lennard-Jones Trans. Farad. Soc. 28 333 ('32)



H_2

Cu_2

Cluster Calculation

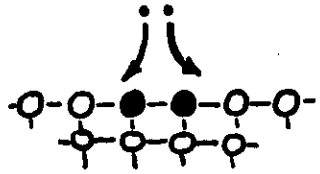


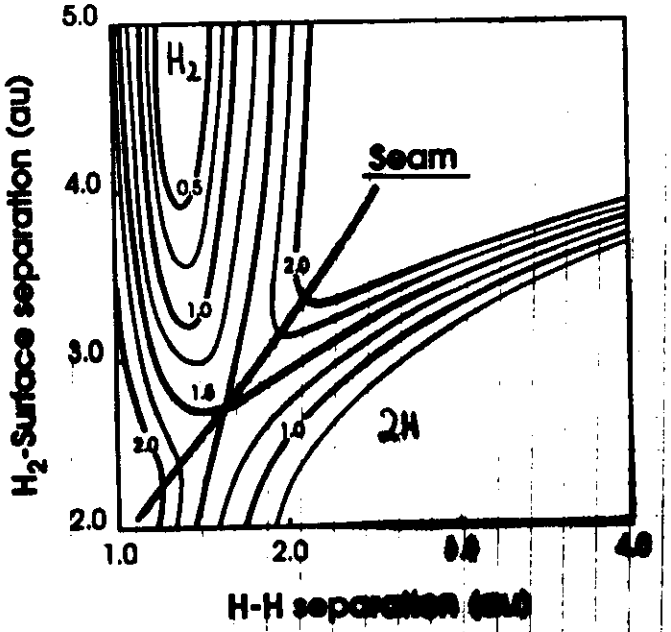
Harris, Holloway, Raman + Yang (JCP soon!)

Figure 2

H_2/Cu(100)

Bridge – top site dissociation





Harris + Anderson PRL 55, 1583 (1985)

Figure 3

Activated Adsorption

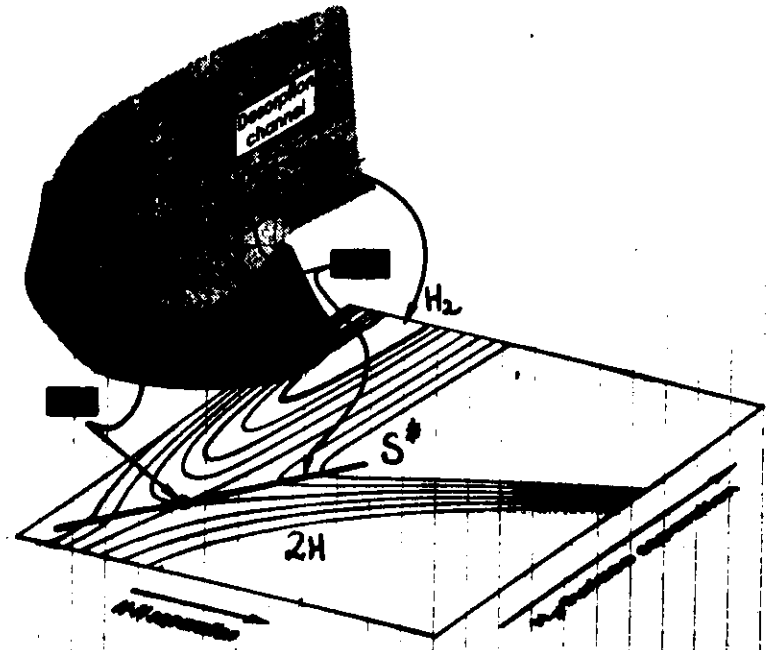


Figure 4