INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

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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
(Lectures III, IV & V)

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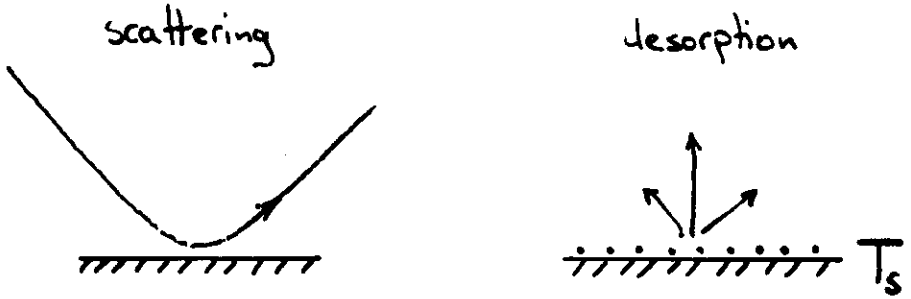
Dynamics of Infrequent Events



$\tau_{scatt} \sim 10^{-12}$ sec

$\tau_{des} \sim 10^{-6}$ sec

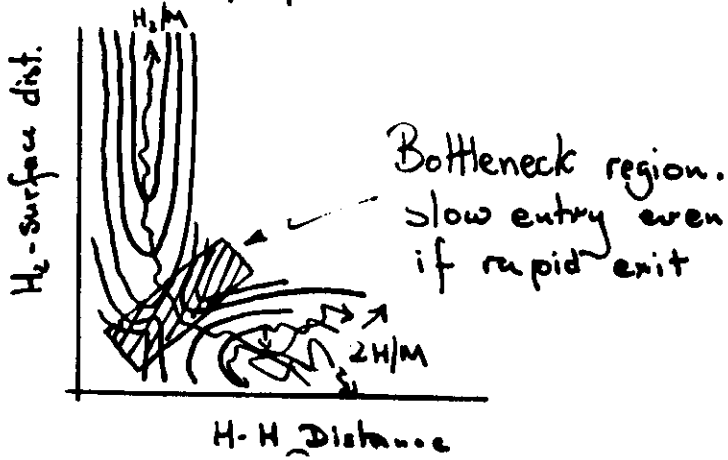
Typically in performing molecular dynamics $\Delta t \sim 10^{-14}$ sec.

→ $n_{scatt} \sim 10^2$ timesteps

→ $n_{des} \sim 10^8$ timesteps

[Wolken JCP 63 4072 (1975)]

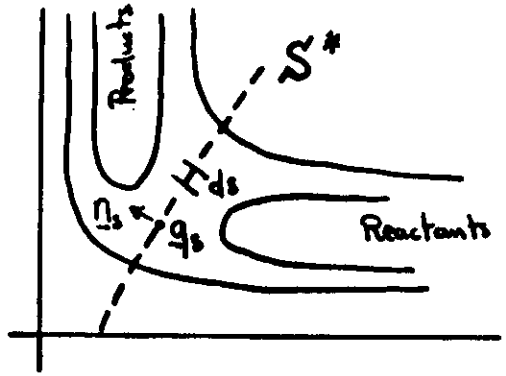
How are infrequent events simulated?



Bottleneck region. slow entry even if rapid exit

Factoring the rate constant.

{Keck Adv. Chem. Phys 13, 85 (1967) + Göran Wahnström}



Equilibrium rate constant

$$k = \frac{1}{Q_{react.}} \int d\underline{p}\, ds\, (\underline{p}\cdot\underline{n}_s)\, \chi_r(\underline{p},\underline{q}_i)\, e^{-H(\underline{p},\underline{q}_i)/kT}$$

- $(\underline{p}\cdot\underline{n}_s)$: adds trajectories passing from reactant → products
- $\chi_r(\underline{p},\underline{q}_i)$: characteristic function which is +1 for a reactive trajectory + 0 otherwise
- $e^{-H(\underline{p},\underline{q}_i)/kT}$: Equilibrium dist^n of reactants

How is this related to k_{TST}?

$k = k_{TST}\,(F)$

k_{TST}: equilibrium processes

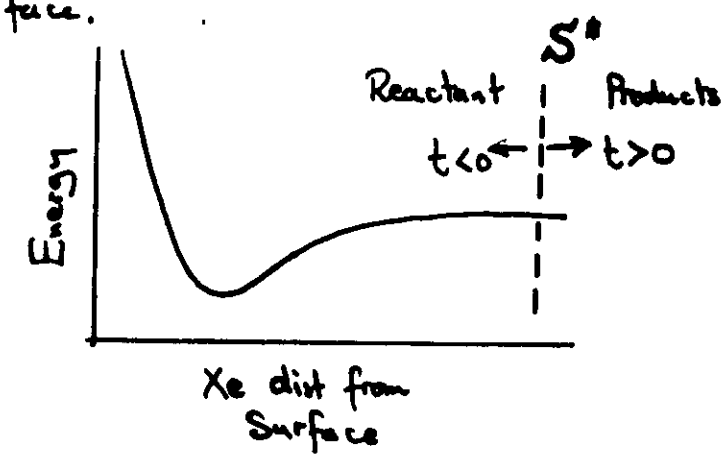
F: dynamic correction factor

Thus, F accounts for all of the complex re-crossing phenomena. It may be evaluated by initiating a swarm of trajectories at s^* and integrating forwards & backwards in time to check for reactive trajectories.

Example

Desorption of Xe/Pt(111) {Grimmelman et al JCP 74 5500 (1981)}

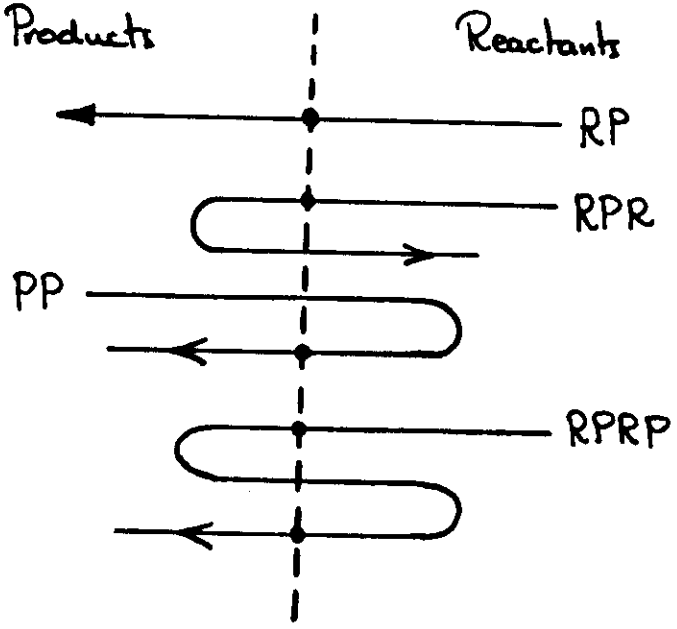
choose s^* to be located far above the surface.



$$k_{TST} = \frac{1}{Q_{react}} \int d\underset{\sim}{p}\, ds\, (\underset{\sim}{p}\cdot\underset{\sim}{n}_s)\, \chi_+(\underset{\sim}{p}, \underset{\sim}{q}, \underset{\sim}{n}_s)\, e^{-H/kT}$$

$$\chi_+(\underset{\sim}{p}, \underset{\sim}{q}, \underset{\sim}{n}) = 1 \quad \underset{\sim}{p}\cdot\underset{\sim}{n} > 0$$
$$= 0 \quad \text{otherwise}$$

Dynamics disappears in this step



clearly $k_{TST} \geq k$

Since at S^* those trajectories with $(\underline{p}\cdot\underline{n}_s)>0$ definitely desorb, there is no need to integrate for $t>0$. One integrates backwards in time to find those which originated as reactants

The problem is to find those trajectories which begin at S^* and evolve backwards in time to stick, by microscopic reversibility therefore:

F = Sticking coefficient! $(z_0 \to \infty)$

$$\Rightarrow k = k_{TST}\, S_0$$

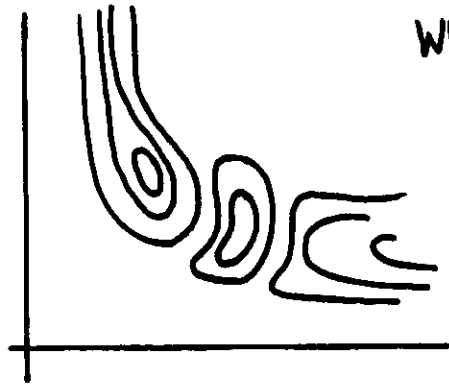
{ Light, Nozieres, J. Phys. 27 1813 (1978) }

By this method 12 orders of magnitude in rate of desorption were calculated.

Example

$H_2/Cu(100)$ { Harris, Holloway, Rahman + Yang JCP }

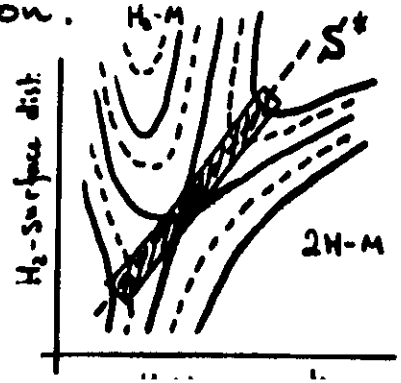
Variational TST:



Where is S^*?

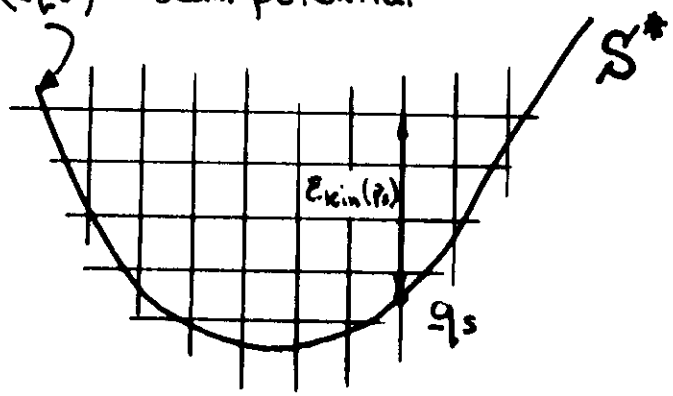
Change S^* and wait for the minimum value of F. If $F=1$ then the crossing surface is traversed only once, $k_{TST} = k$.

For H_2/Cu there is a very well defined bottleneck for the reaction.



Initiate a swarm of trajectories along S^*, and record the probability distribution functions $P_{vib}(\varepsilon)$, $P_{trans}(\varepsilon)$ and $P_{rot}(\varepsilon)$.

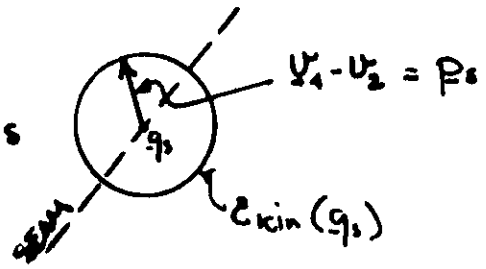
$V_s(q_s)$ = seam potential



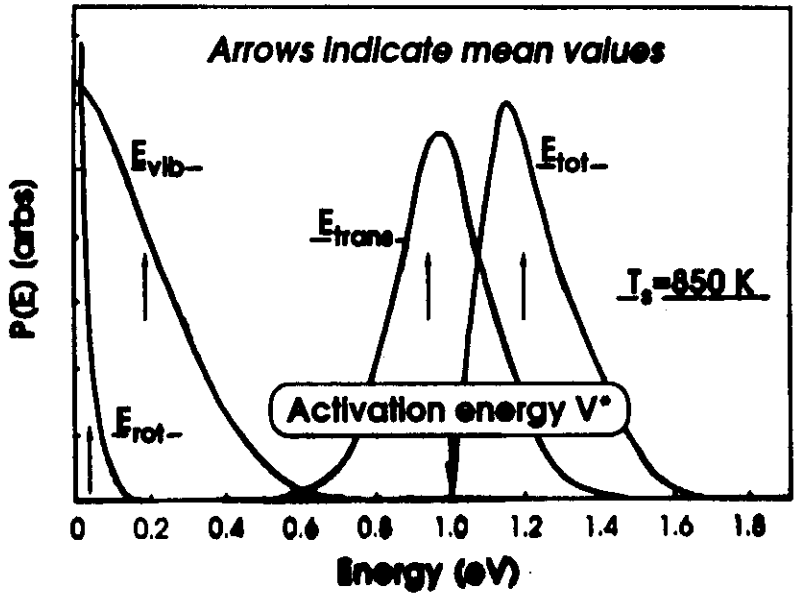
$$P(q_s, p_s) \sim \exp\left[-\left[V_s(q_s) + \varepsilon_{kin}(p_s)\right]/kT_s\right]$$

$$S^* \Rightarrow \frac{dq_s}{ds} = \frac{\nabla V(q_s)}{|\nabla V(q_s)|}$$

average over relative H-atom velocities



Probability distributions



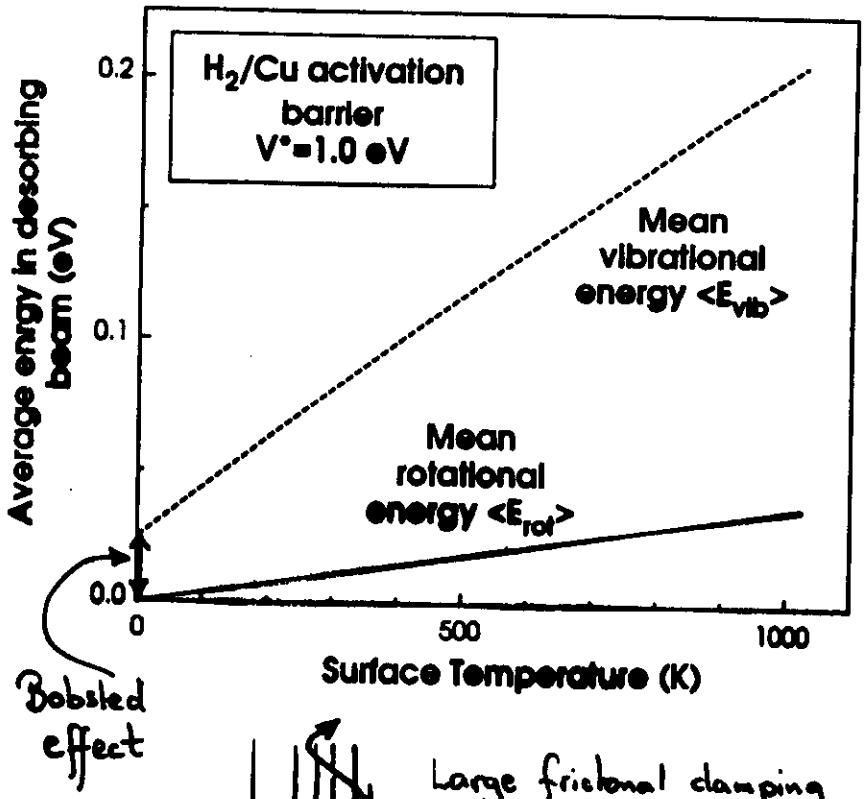
$P(E_{rot})$ - almost thermal at T_s

$P(E_{vib})$ - dynamically enhanced

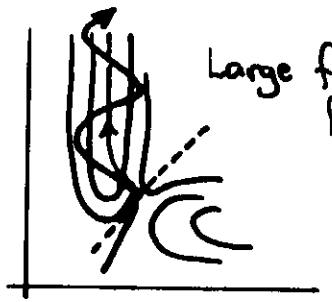
$P(E_{trans})$ - dynamically enhanced.

Figure 5

Temperature distributions of mean energies



Bobsled effect

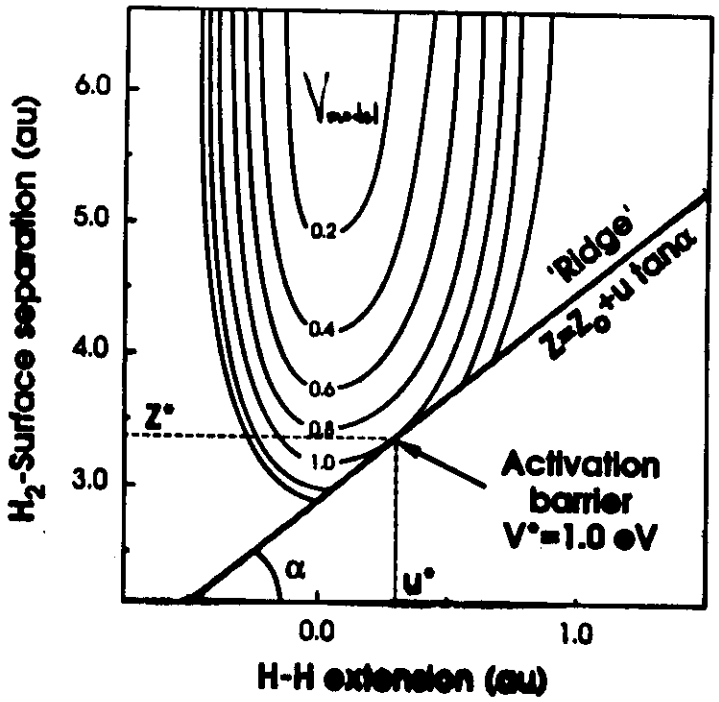


Large frictional clamping [unlikely m_H/m_{Cu}]

Figure 6

H_2/Cu (100) Model Potential

(The line on a hill model!)



$$V_{model}(u,z) = V_{Harmonic}(u) + V_0 e^{-\lambda z}$$

Figure 7

Associative Desorption $H_2/Cu(100)$

Potential in "exit channel":

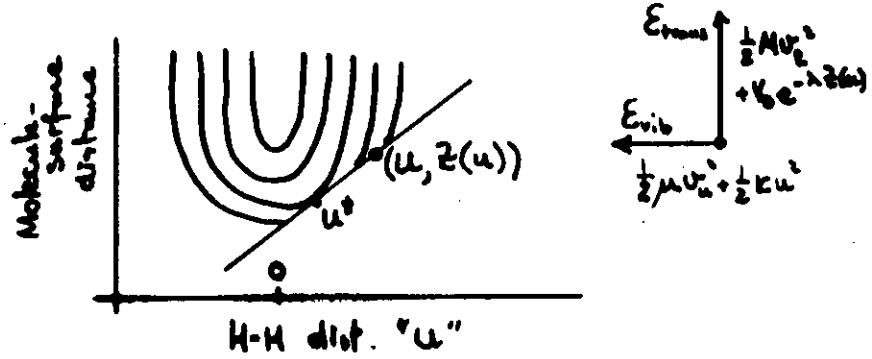
$$V(z,u) = V_0 e^{-\lambda z} + \frac{1}{2} k u^2$$

Seam:

$$Z(u) = Z_0 + u \tan\alpha$$

Transition state (col):

$$u^* = \sqrt{\frac{1}{\lambda^2 \tan^2\alpha} + \frac{2E_{ext}}{k}} - \frac{1}{\lambda \tan\alpha}$$



Velocity dist^n

$$p(u, v_z, v_u) \sim [v_z - v_u \tan\alpha]\, e^{-\beta\left[\frac{1}{2}Mv_z^2 + \frac{1}{2}\mu v_u^2 + V(Z(u),u)\right]}$$

$$\Theta[v_z - v_u \tan\alpha]$$

Mean translational energy (normal)

$$\langle\langle E_\perp \rangle\rangle = E_{ext} - \tfrac{1}{2} k u^{*2} + kT_s \left\{ \frac{1 + 2\tan^2\alpha}{1 + 4\tan^2\alpha} \right\}$$

Mean vibrational energy

$$\langle\langle E_{vib} \rangle\rangle = \tfrac{1}{2} k u^{*2} + \tfrac{1}{2} kT_s \left\{ \frac{1 + 8\tan^2\alpha}{1 + 4\tan^2\alpha} \right\}$$

Comments:

> At $T_s = 0$ only ptcles at the col contribute

> Orientation of the crossing seam S^* very important:

$$\left.\begin{aligned} \langle\langle E_\perp \rangle\rangle &= kT_s + E_{ext} \\ \langle\langle E_{vib} \rangle\rangle &= \tfrac{1}{2} kT_s \end{aligned}\right\} \alpha = 0$$

"Van Willigen results"

> Displaced transition state significant.

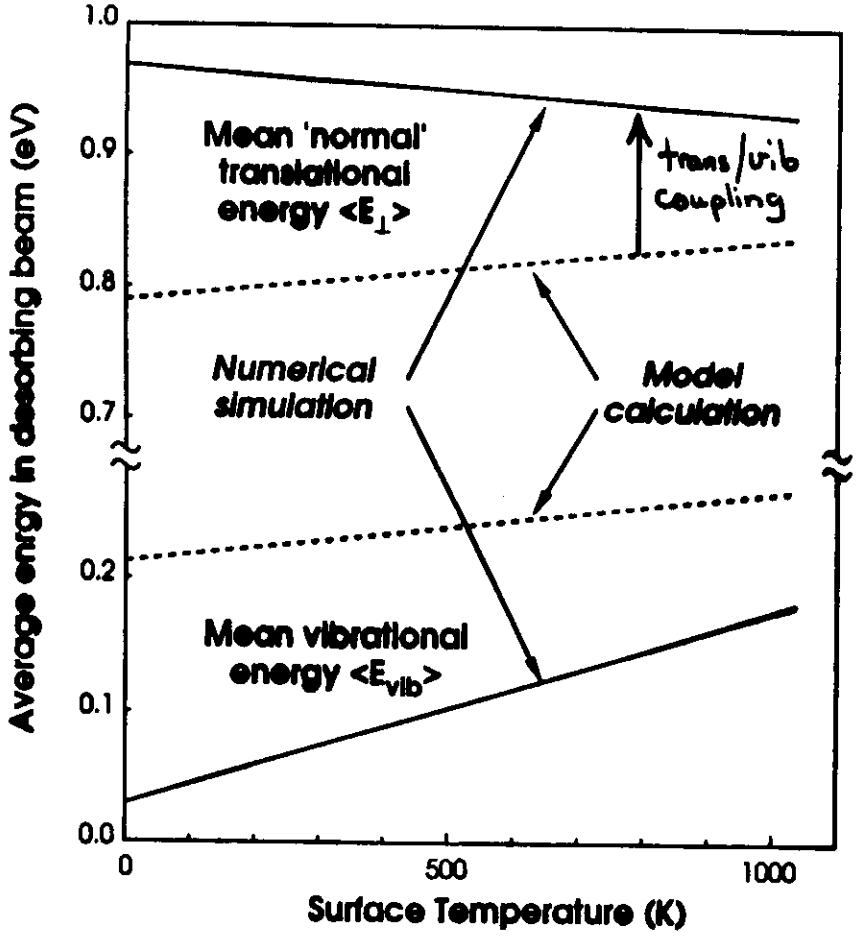
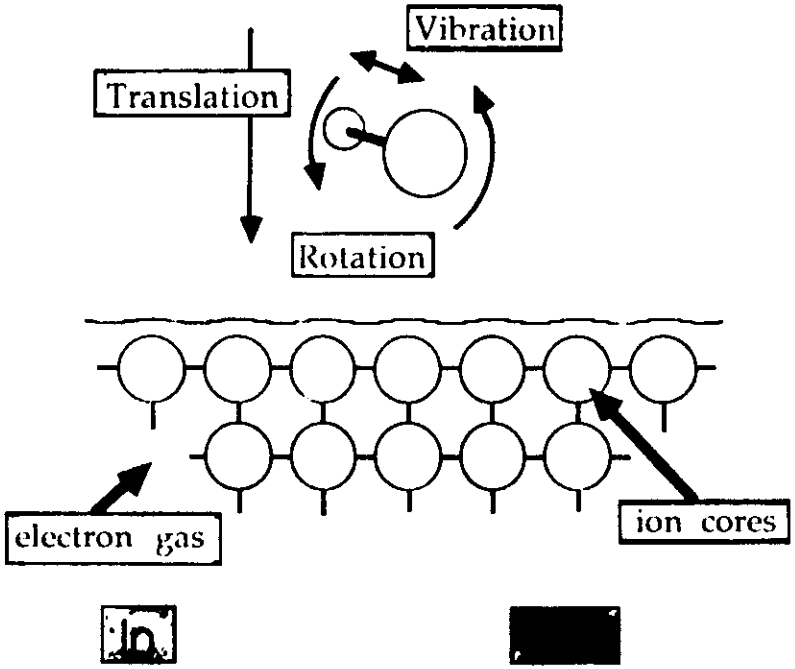


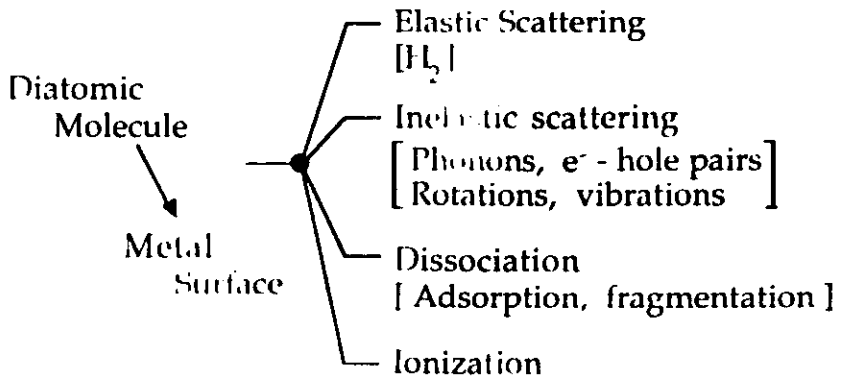
Figure 8

CHARGE-TRANSFER, VIBRATIONAL EXCITATION AND DISSOCIATIVE ADSORPTION IN MOLECULE-SURFACE COLLISIONS.

- *Introduction*
- *Some recent experiments*
- *Concepts in gas-surface interactions*
- *Translation-vibrational excitation*
  - *quantum*
  - *classical*
- *Collisional dissociation*
- *Dissociative adsorption*
- *Conclusions*

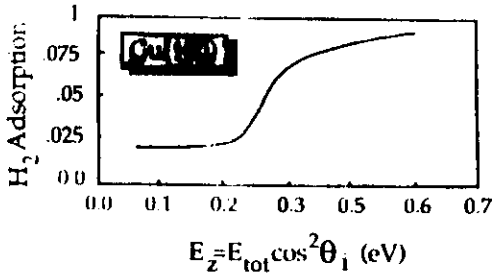
Gas-Surface Scattering



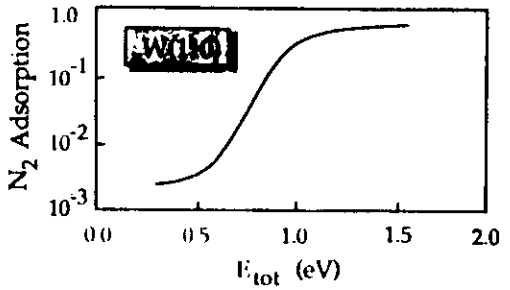


➤ Dissociative adsorption

M.J. Cardillo, M. Balooch, and R.E. Stickney, Surf. Sci. **44**, 358 (1974)

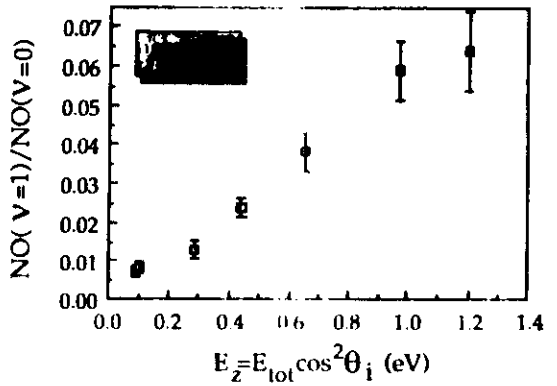


D.J. Auerbach, H.E. Pfnür, C.T. Rettner and J.E. Schlaegel, J. Chem. Phys. **81** 2515 (1984)



➤ Vibrational excitation.

C.T. Rettner, F. Fabre, J. Kimman and D.J. Auerbach, Phys. Rev. Lett. **55** 1904 (1985)

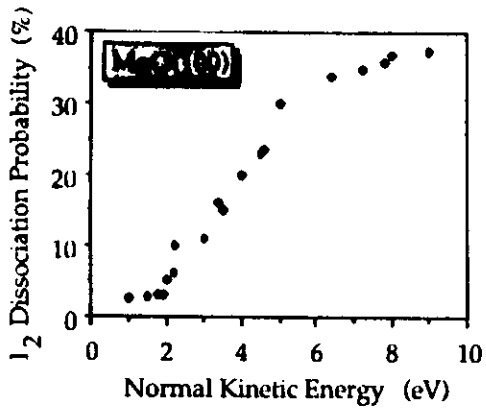


5.

4.4

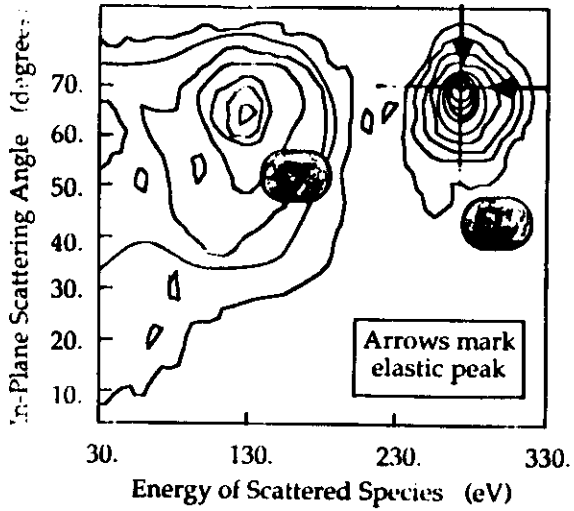
Collision induced dissociation

E. Kolodney and A. Amirav,
J. Chem. Phys. 79, 4648 (1983)



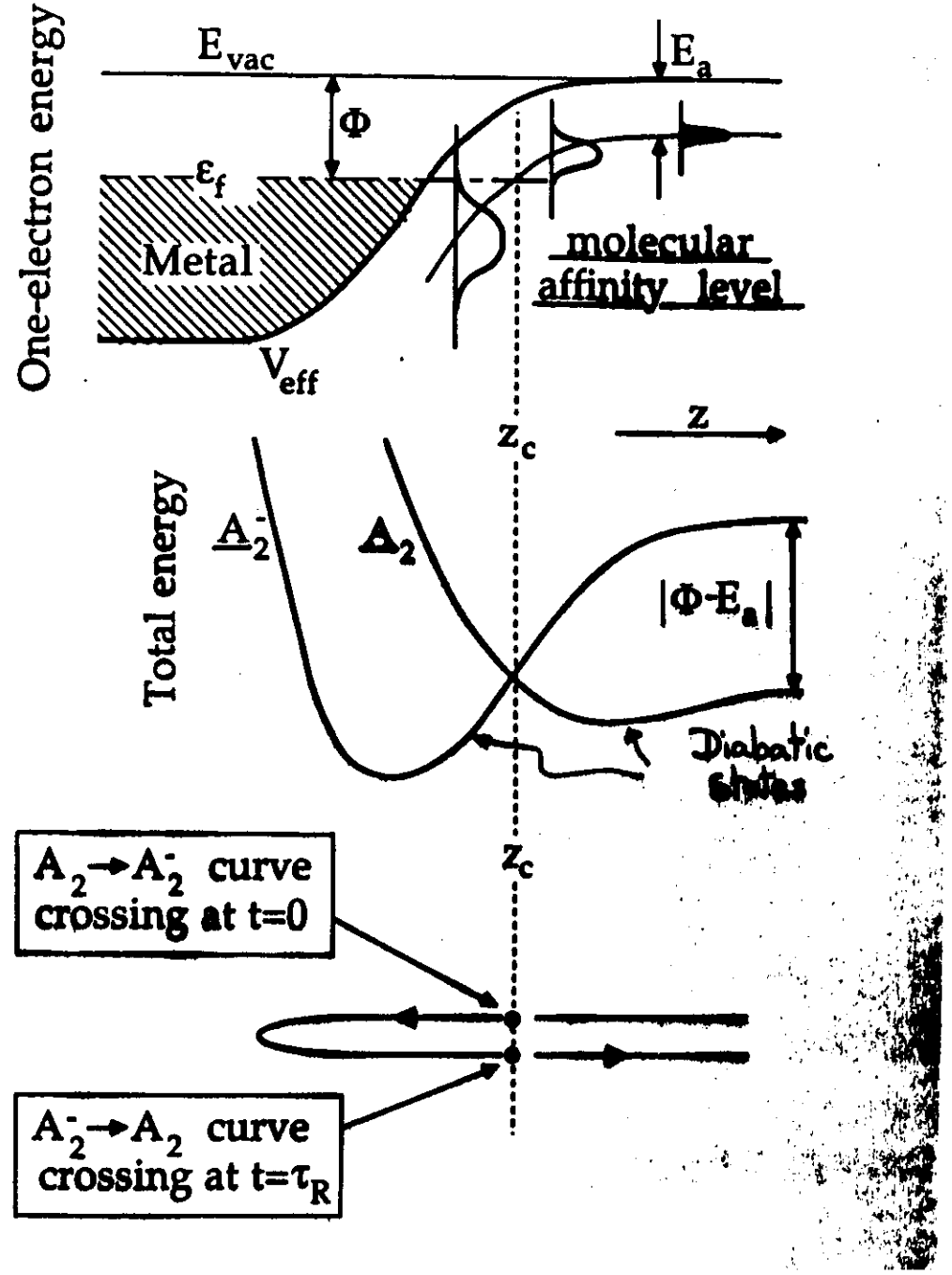
Surface harpooning

Pan Haochang,
Tom Horn
and Aart Kleyn,
Phys. Rev. Lett. 57,
3035 (1986)

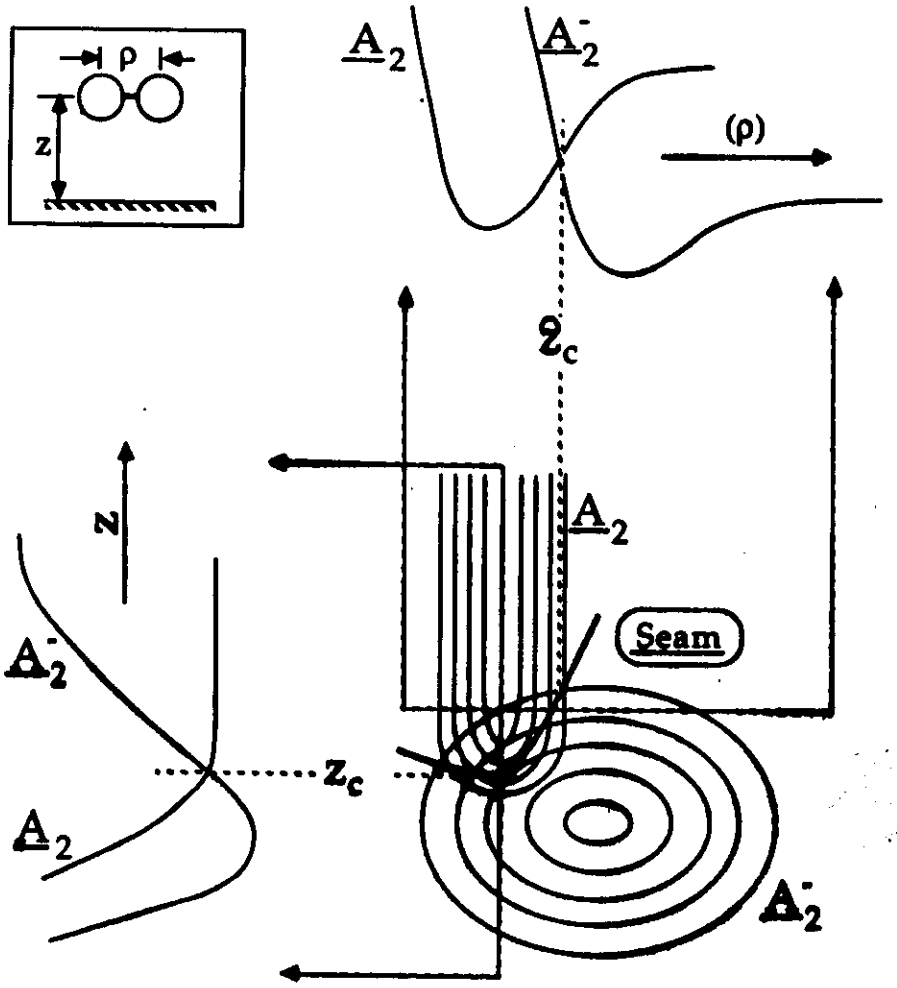


7.

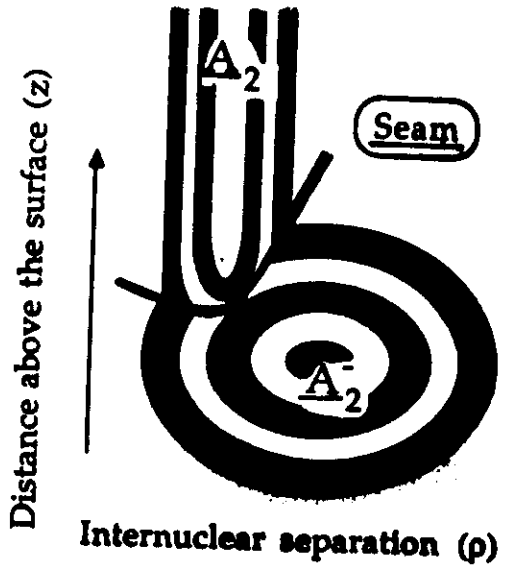
7.5



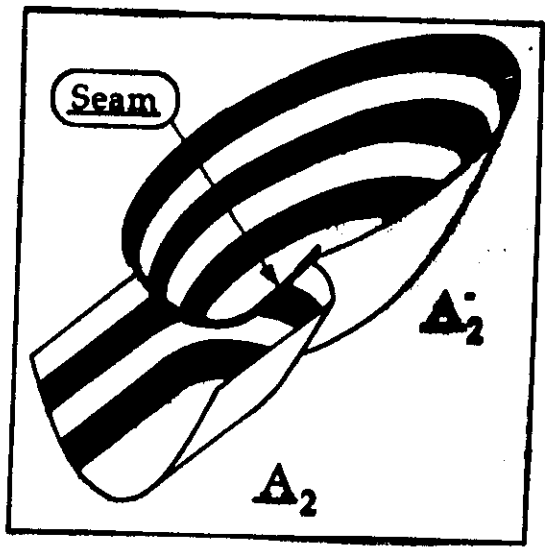
Diatomic-Metal Potential Energy Surface



Classical Scattering



"Adiabatic States"



Translation → Vibration Conversion in Diatomic-Surface Scattering

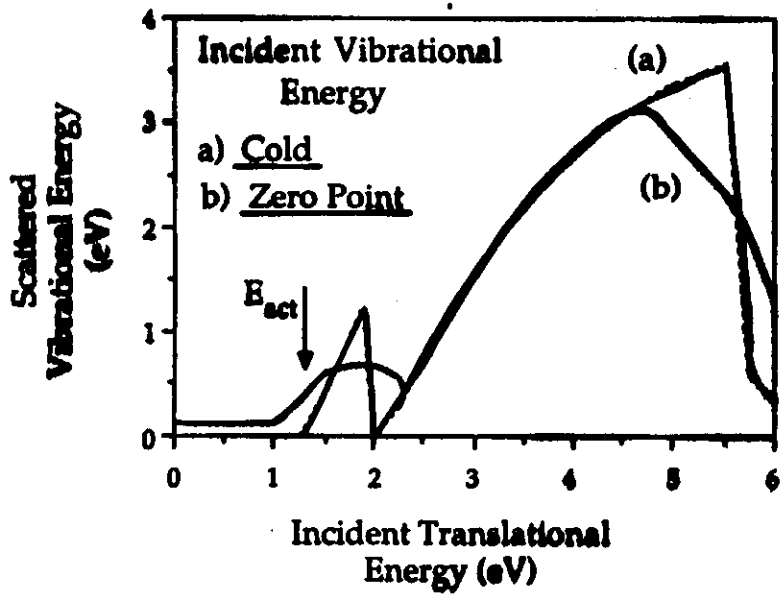
For a given set of initial conditions, solve the classical equations of motion,

$$\dot{q}=\frac{\partial H}{\partial p},\quad \dot{p}=-\frac{\partial H}{\partial q},$$

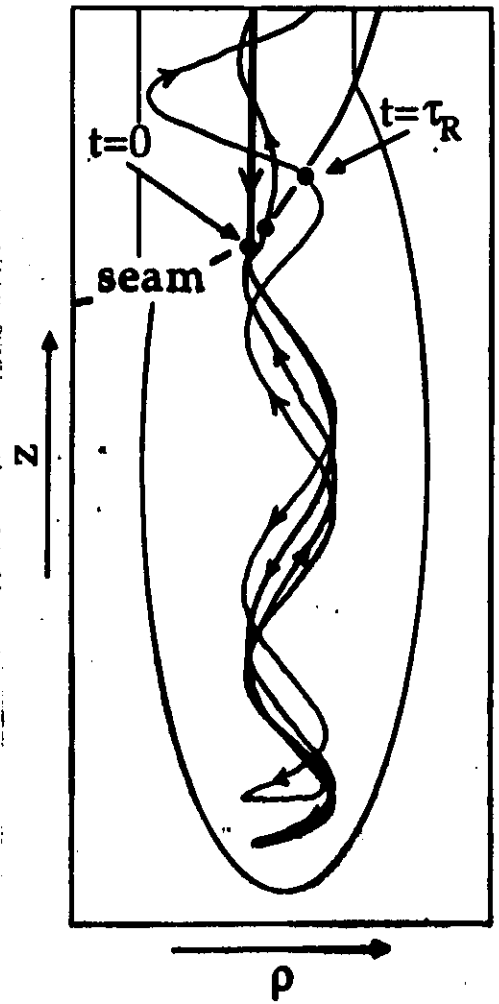
under the assumption that an $A_2 \rightarrow A_2^-$ transition occurs with unit probability. "adiabatic"

(E_z^f, E_ρ^f)

(E_z^i, E_ρ^i)



Origin of Resonances in T → V Scattering



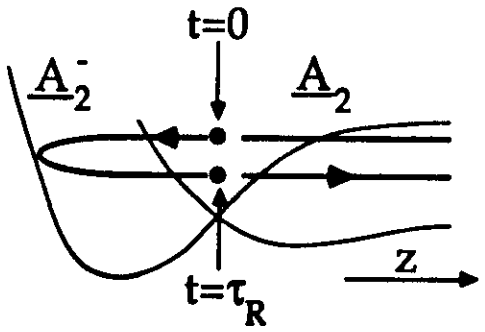
If $\tau_R = n\tau_p$ then for any trajectory, $E_z^i = E_z^f$ and $E_\rho^i = E_\rho^f$.

"Frequency Comensurability"

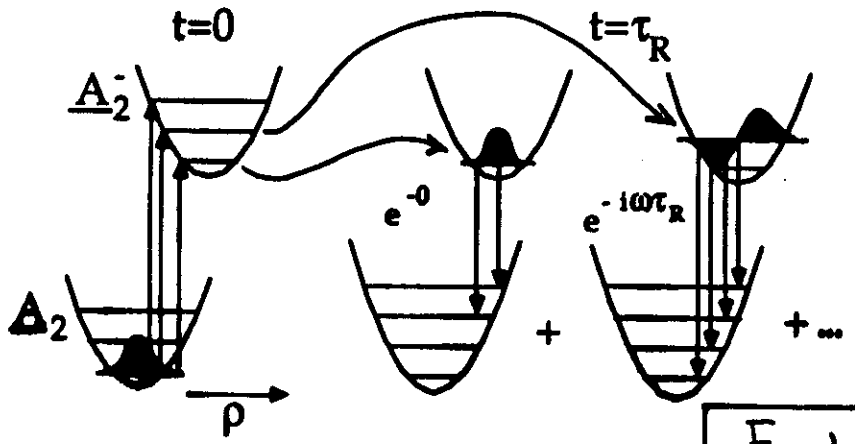
- Gives rise to resonances
- Topological result

S. Holloway and J.W. Gadzuk, Surf. Sci. 152-153, 826 (1985); J. Chem. Phys. 82, 5289 (1985)

Translational Degree of Freedom



Vibrational Degree of Freedom



Franck-Condon Factors

Probability of emerging in the n^{th} vibrational state:

$$P_n = \left|\sum_{\tilde{m}} \langle n|\tilde{m}\rangle e^{-i\varepsilon_{\tilde{m}}\tau_R}\langle\tilde{m}|0\rangle\right|^2$$

Wavepacket Dynamics

Since the vibrational states $|\tilde{m}\rangle$ form a complete set,

$$\sum_{\tilde{m}} |\tilde{m}\rangle e^{-i\varepsilon_{\tilde{m}}\tau_R}\langle\tilde{m}|0\rangle = e^{-iH_{A_2^-}\tau_R}|0\rangle$$

$$\equiv |\phi_o(\tau_R)\rangle$$

where $|\phi_o(t)\rangle$ is a time-dependent wavepacket propagating for τ_R on $H_{A_2^-}$.

Then, $P_n = |\langle n|\phi_o(\tau_R)\rangle|^2$,

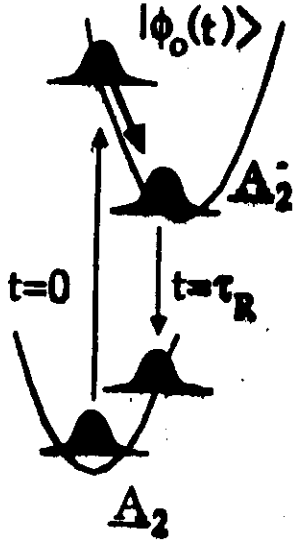
$$= \exp(-\beta(\tau_R))\frac{\beta^n(\tau_R)}{n!}.$$

Where

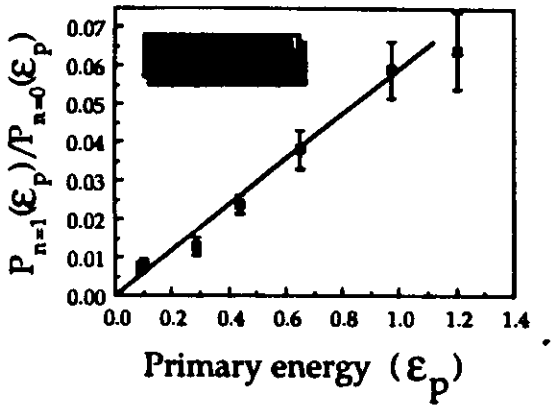
$$\beta(\tau_R) = 2[1-\cos\tilde{\omega}\tau_R(\varepsilon_p)]\beta_o$$

and $\beta_o = \dfrac{\Delta R_{eq}^2 \mu\omega}{2\hbar}$.

"Poisson Distribution"



Vibrational Excitation In Gas-surface Scattering.



From before,

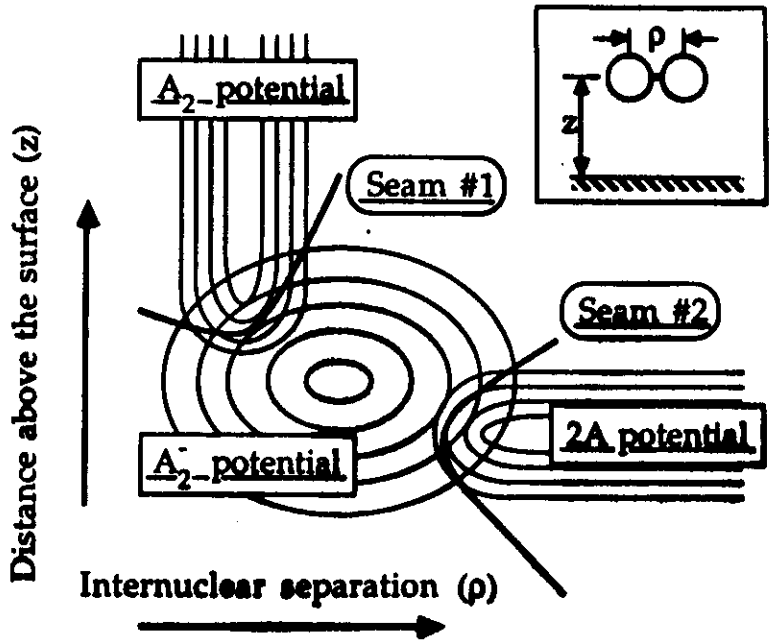
well depth

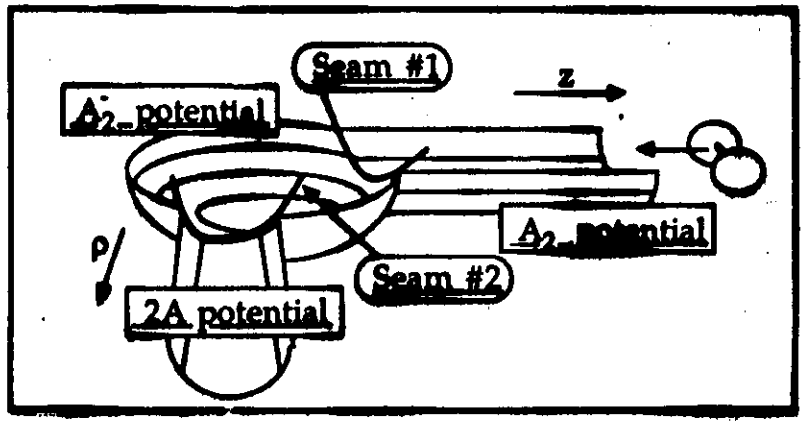
$$\frac{P_{n=1}(\varepsilon_p)}{P_{n=0}(\varepsilon_p)} = 2\beta_o'(\Delta n)\left[1+\cos\left\{2\sin^{-1}\left[\frac{\varepsilon_d}{\varepsilon_d+\varepsilon_p}\right]\right\}\right]$$

For the case of NO scattering , the charge transfer (Δn) will be < $1e^-$. An estimate may be obtained from E_{aff} and Φ.

J.W. Gadzuk and S.Holloway, Phys. Scr. 32 ,413 (1985); Phys. Rev. B 33, 4298 (1986).

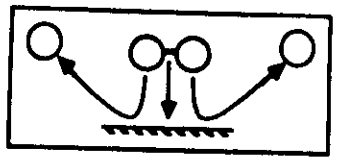
Dissociative Adsorption



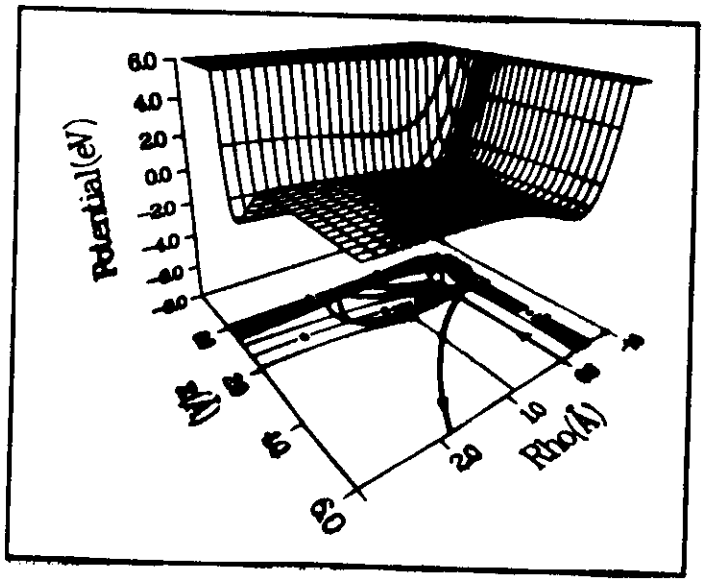


Collision-Induced Dissociation

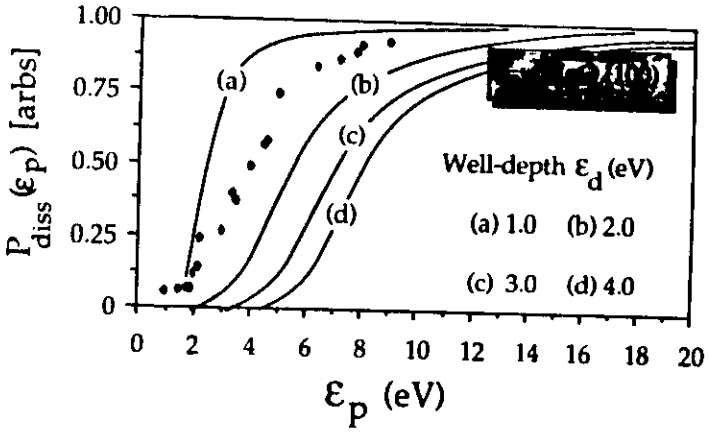
If in a surface encounter enough energy is transfered to the vibrational coordinate, the molecule will dissociatively scatter.



Model adiabatic potential energy surface for I_2 scattering.

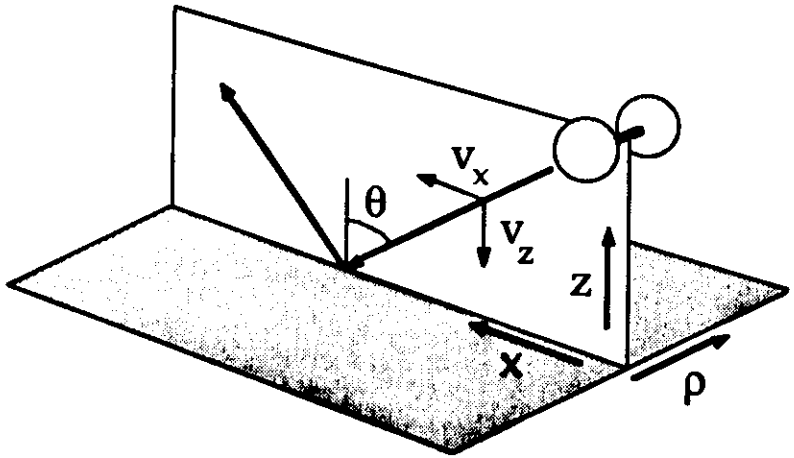


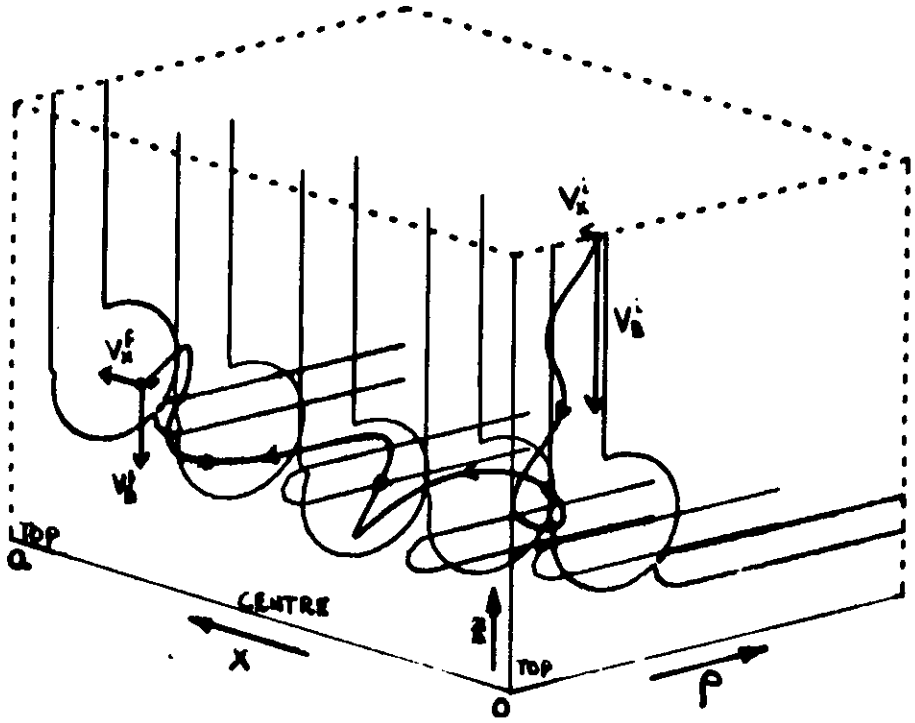
- Wavepacket analysis
- Dissociation occurs if $E_\rho^f > \varepsilon_{diss}$ (=1.54 eV for I_2)
- $$P_{diss}(\varepsilon_p) = P_{L\text{-}Z} \int_{\varepsilon_{diss}}^{\infty} \frac{dP[\tau_R(\varepsilon_p)]}{d\varepsilon} d\varepsilon$$



S. Holloway and J.W. Gadzuk, J. Chem. Phys. 84, 3502 (1986)

E_{total} vs E_{normal} Scaling in Dissociative Adsorption





A Time Dependent Quantum Approach to Gas-Surface Scattering.

Introduction

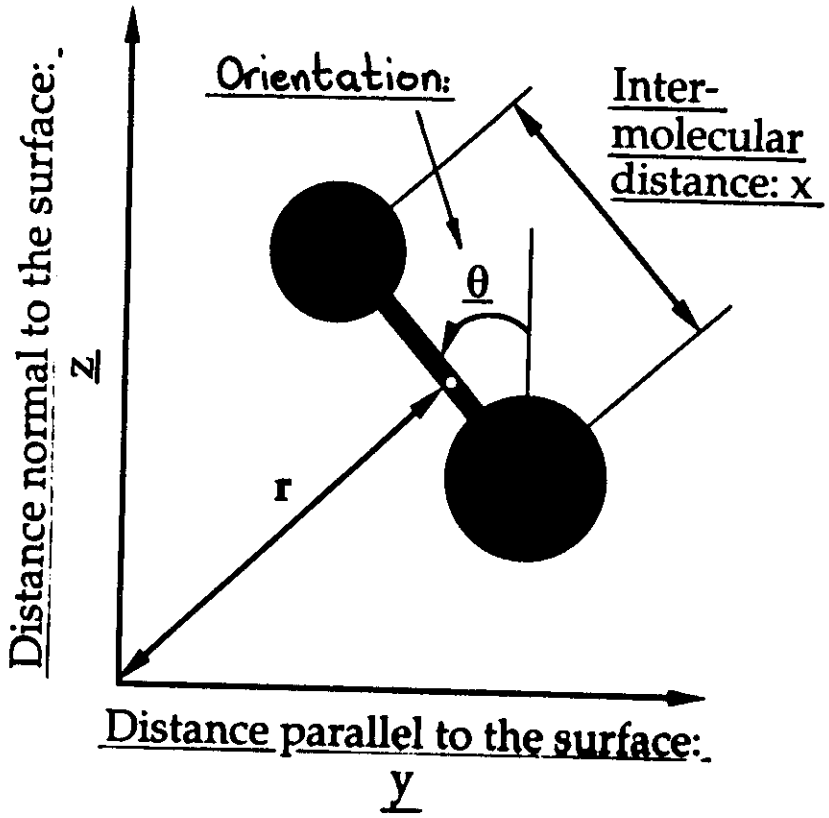
- ⋆ *Microscopic interactions*
- ⋆ *Degrees of freedom*
- ⋆ *Experimental observation*

The Potential-Energy-Surface

- ⋆ *Selected cuts*
- ⋆ *Quantum vs. classical mechanics*

Examples and Results

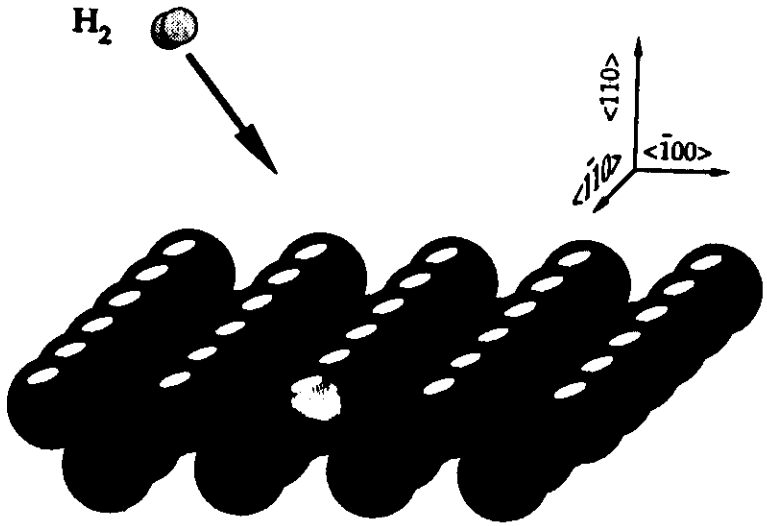
- ⋆ *Molecular diffraction and reaction*
- ⋆ *Vibrationally enhanced reactivity*
- ⋆ *A new look at rotational scattering*



- Is it of value to examine the total problem in terms of subsets of coordinates?

- In experiments, are there obvious *useful* and *useless* motions to consider?

For low energy H_2 scattering from surfaces, the scattered molecules display little coupling to either intermolecular rotations (θ) or substrate excitations (Q). *For some metal surfaces, however, H_2 molecules dissociatively adsorb and diffract.* For fcc (110) surfaces the surface corrugation is in some cases 1-dimensional.



An fcc (110) surface (Cu, Ni, Ag)

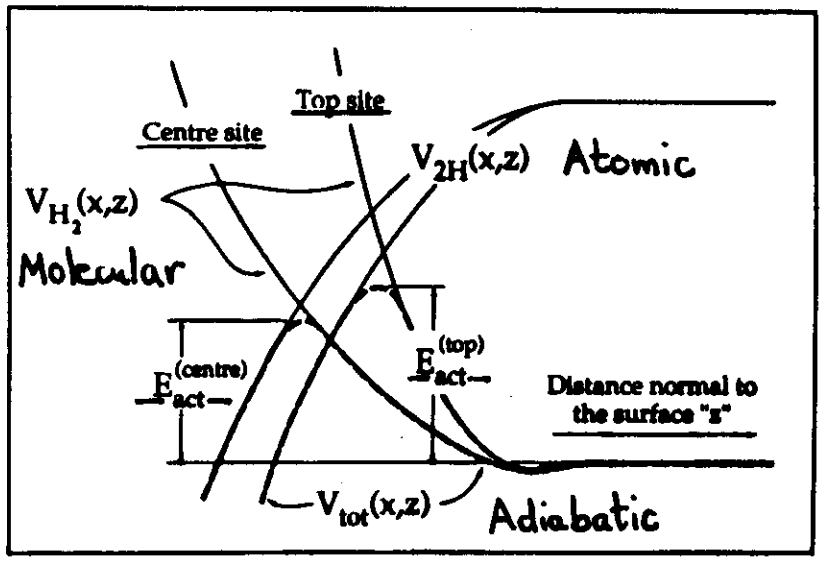
Karikorpi, S.H. Henriksen + Nørskov, Surf. Sci 179 L41 (1987)

H_2 Diffraction

PES: Essentialy a two-dimensional generalization of the Lennard-Jones Model.
J.K. Nørskov et al. Phys. Rev. Lett. 76, 257 (1981).

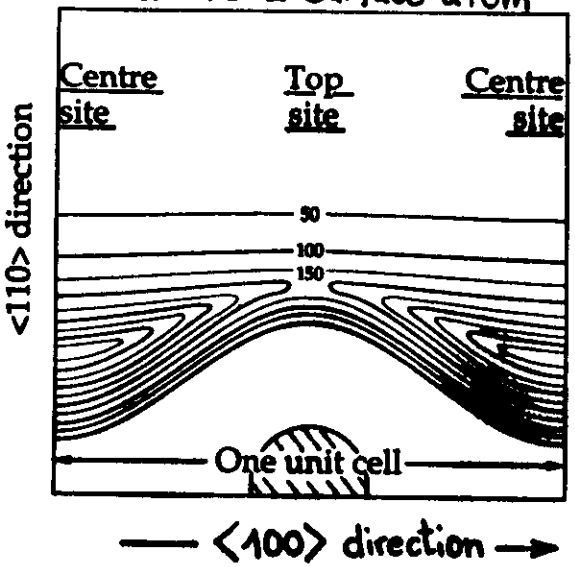
Is it possible, by inverting (elastic) diffraction data to determine where in the surface unit cell the reactive sites are?

"Activated adsorption"

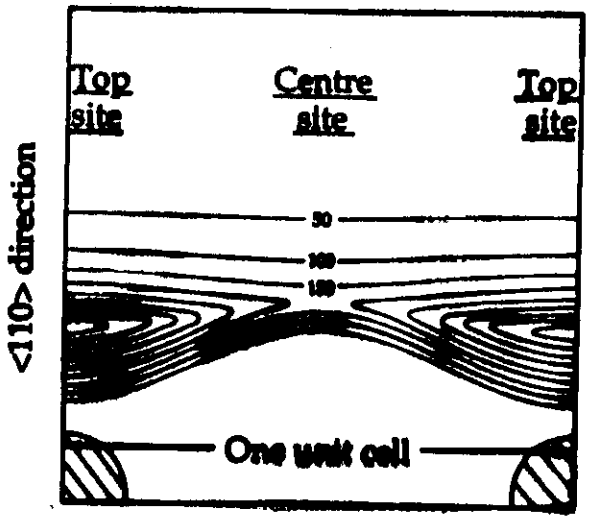


Halstead + S.H. J. Chem. Phys (June 1988)

PES with transition state above a surface atom



Transition state between atoms



Calculational Technique

Coupled channels method.

Expand the V(r) and ψ(r) in surface reciprocal lattice vectors and diagonalize the time independent Schrödinger equation.

+ *An established technique.*
+ *Computationally straightforward.*

- *Expensive for highly structured PES.*
- *Difficult to include substrate motion.*

Time dependent wavepacket scattering.

Put V(r) onto a grid in the region of strong interaction. Propagate the (known) initial state wavefunction in time using:

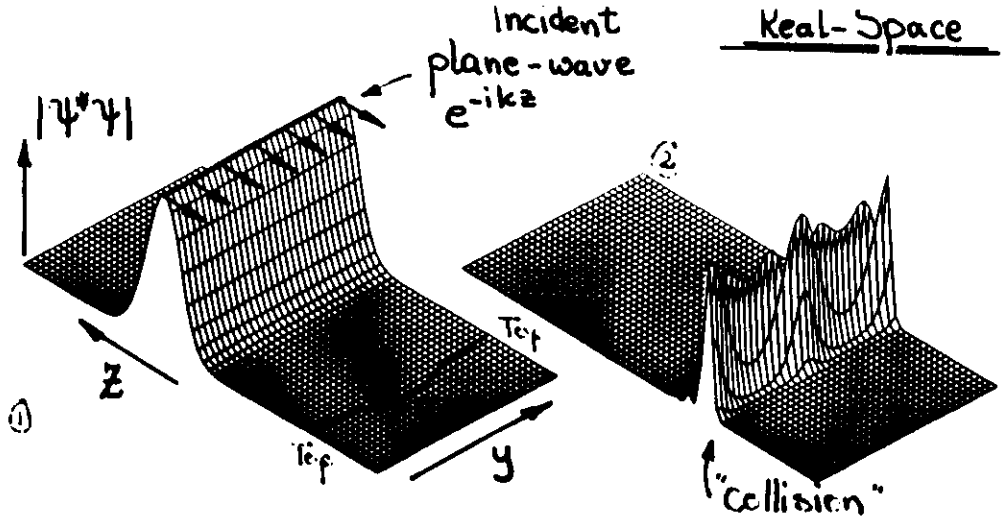
$$|\psi(r,t)\rangle = \exp(-iHt)\,|\psi(r,0)\rangle$$

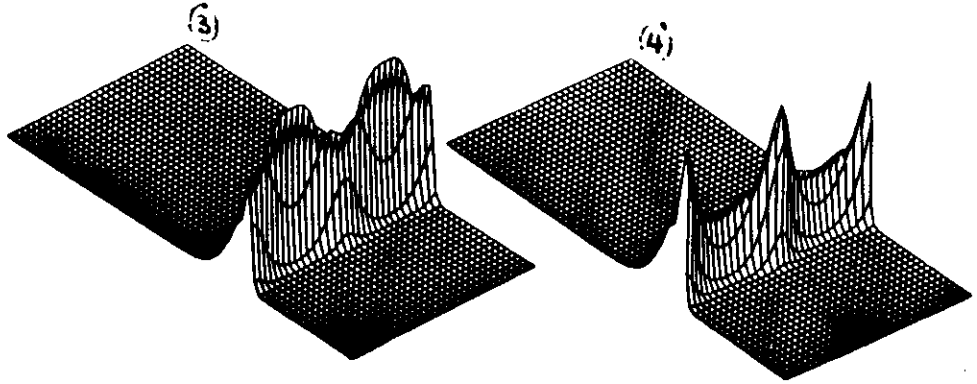
+ *No limitations due to form of PES.*
+ *Time of calculation independent of PES topology.*
+ *Time evolution is very insightful.*
+ *Inclusion of substrate motion possible using semiclassical methods.*

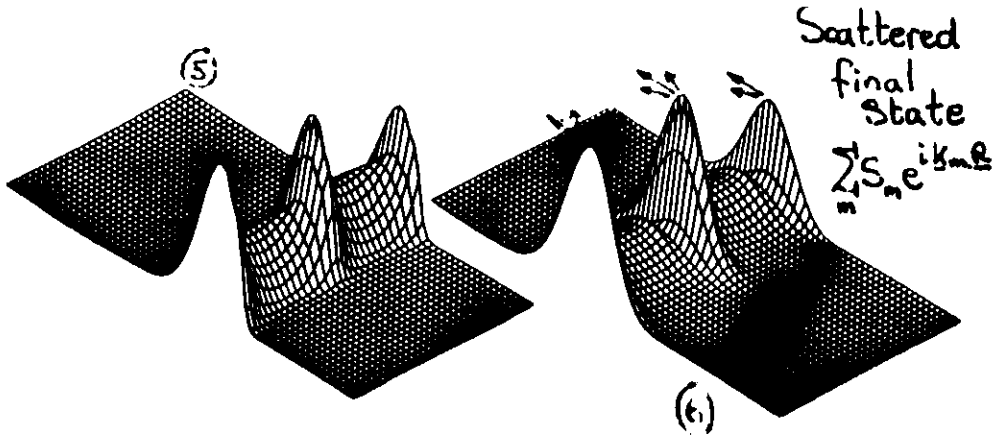
M.D.Feit et al. J. Comput. Phys. 47, 412 (1982).

14.

5.8

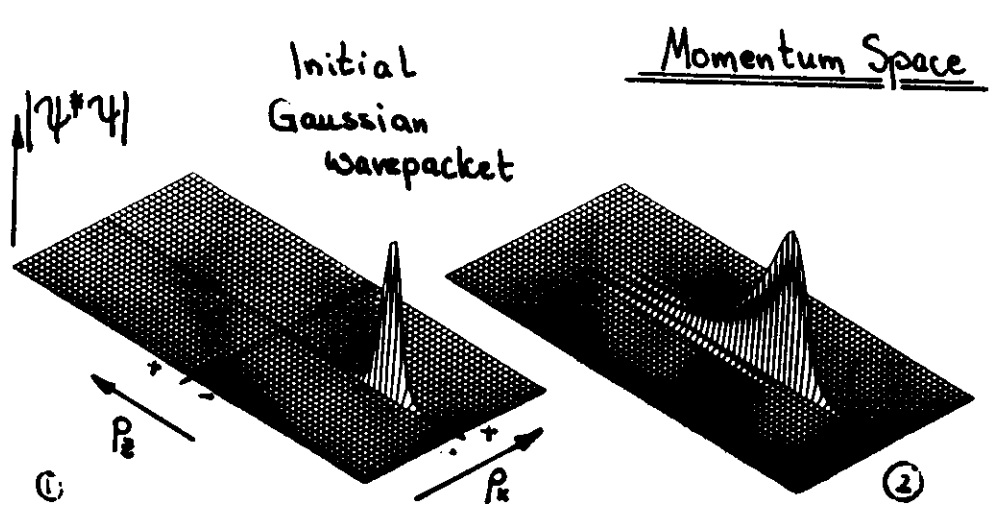

Real-Space
Incident plane-wave e^{-ikz}
$|\psi^*\psi|$
z
y
Tef
Tef
"collision"
①
②

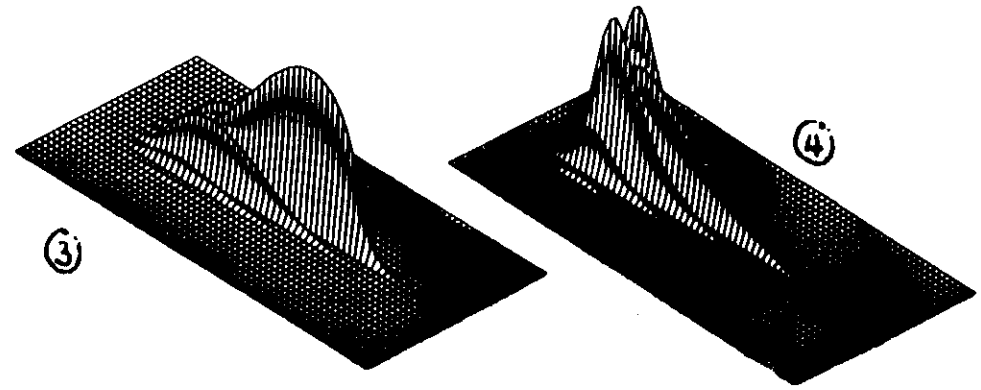

③
④

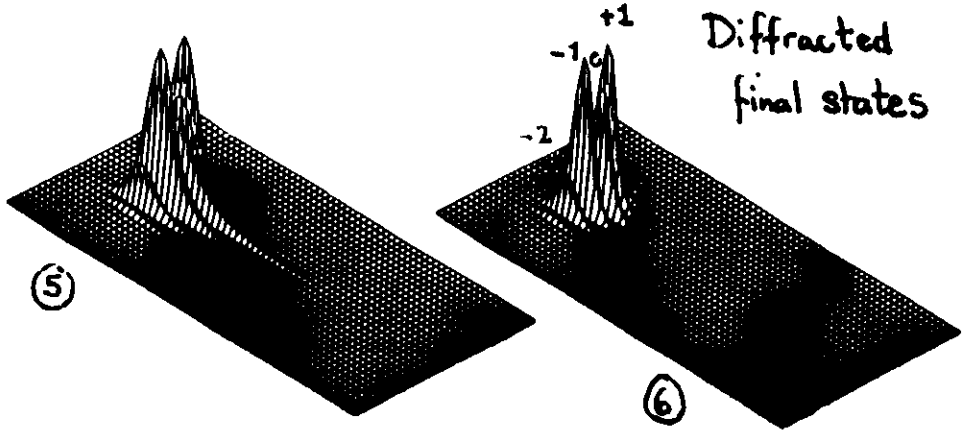

Scattered final state
$\sum_m S_m e^{ik_m R}$
⑤
⑥

15.

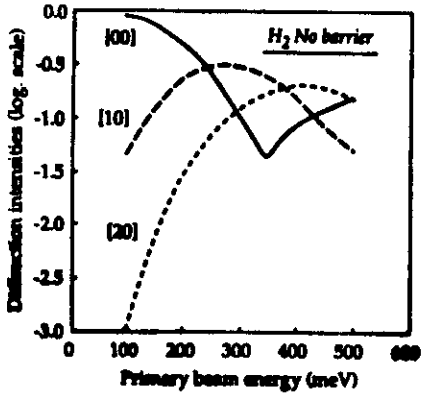
5.9

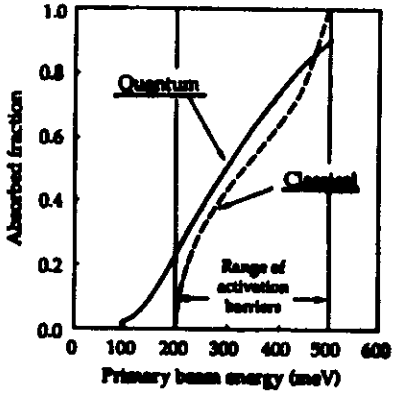

Momentum Space
Initial Gaussian wavepacket
$|\psi^*\psi|$
p_z
p_x
①
②


③
④

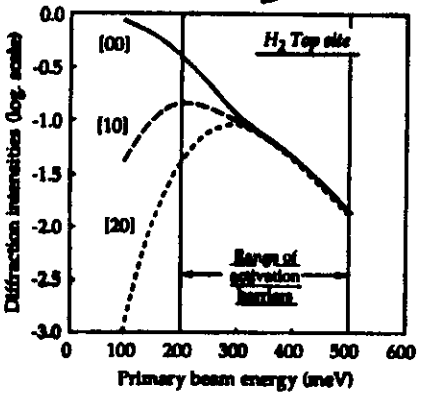

Diffracted final states
+1
-1
-2
⑤
⑥

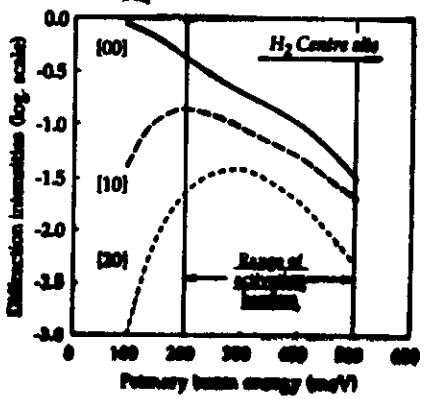
Diffractive-Reactive Scattering H_2/Cu(110)





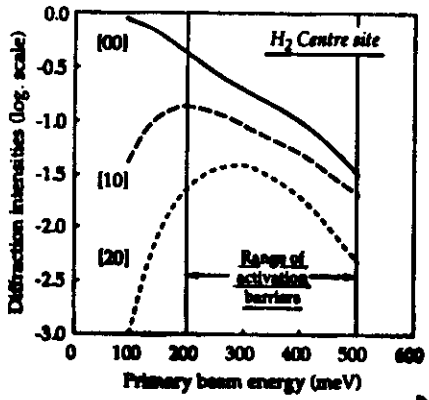
Characteristic behaviour

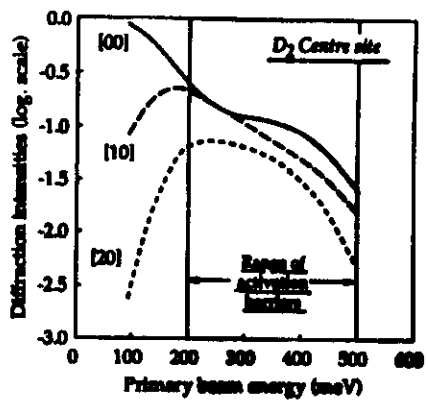




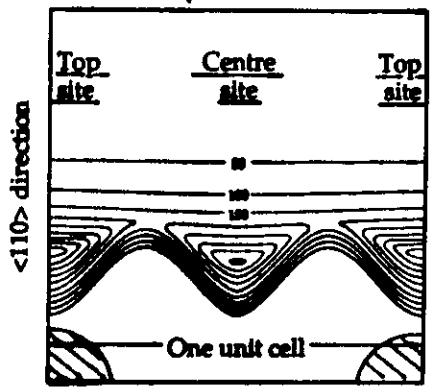
Isotope Effects

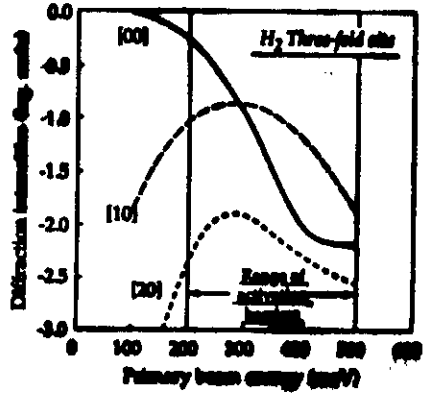
H_2 D_2



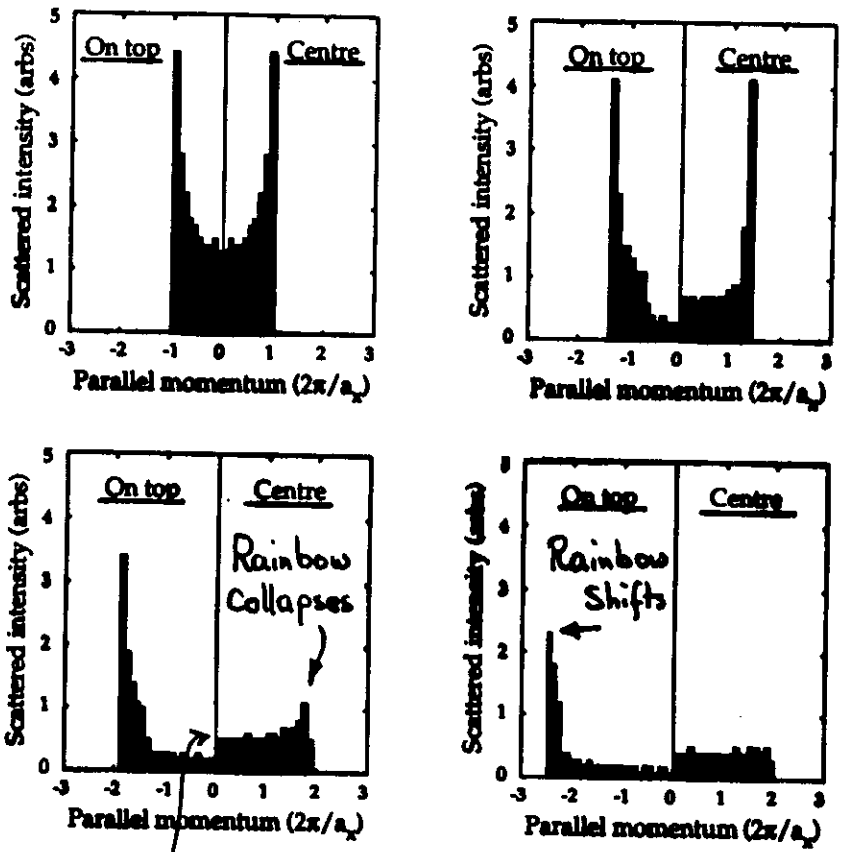


Multiple trans. states !



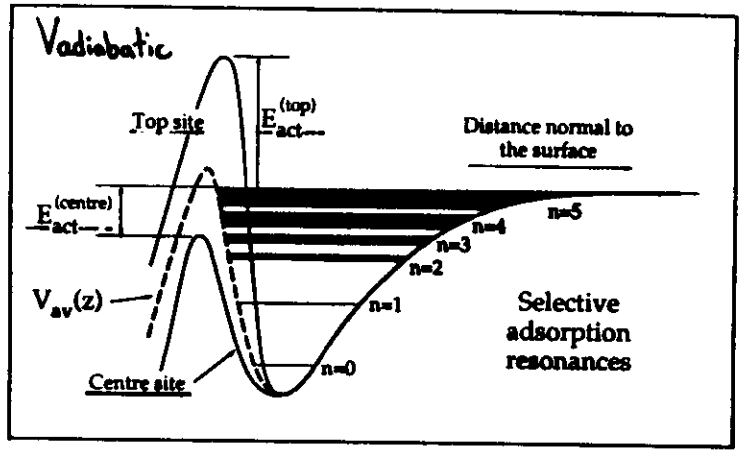


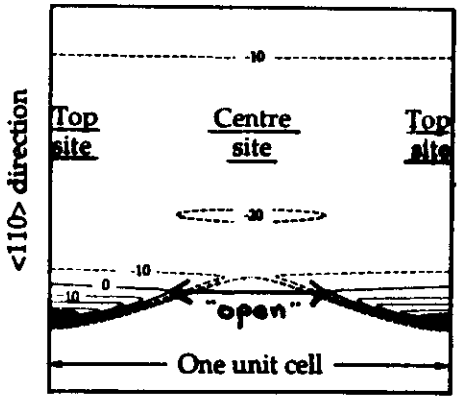
Classical Scattering



Specular drops.

Non-Activated Adsorption





This represents a possible PES for H2 interacting with a transition metal surface which catalyses dissociation.

Selective adsorption ⟺ Sticking ??

COMMUNICATIONS

Effect of vibrational energy on the dissociative chemisorption of N_2 on Fe(111)

C. T. Rettner and H. Stein[a)]
IBM Almaden Research Center, K33/801, 650 Harry Road, San Jose, California 95120-6099

(Received 27 March 1987; accepted 24 April 1987)

Dissociative chemisorption is often associated with a sizable activation barrier, making it the rate-limiting step in many industrially important catalytic systems. A particularly good example is the Haber–Bosch synthesis of ammonia from N_2 and H_2 over iron-based catalysts, where reaction is limited by the dissociation of the N_2.[1,2] Model studies have focused on the N_2/Fe(111) system,[2–4] which has an initial dissociative chemisorption probability of $\sim 10^{-4}$.[5] Despite considerable progress in determining the thermodynamic and kinetic parameters of this system,[5] little is currently known about its detailed dynamics. Here we report the results of a molecular beam study in which we have compared the relative efficacies of kinetic and vibrational energy in activating this process.

The experimental apparatus and techniques employed are similar to those described previously.[6–8] Here we summarize our approach with emphasis on features peculiar to the present system. Supersonic N_2 beams are directed at an Fe(111) crystal mounted in a UHV chamber on a manipulator which permits control of the incidence angle and surface temperature. Sputter–anneal cycles were employed to maintain a clean surface,[5] and the sample was previously exposed to extensive nitrogen dosing to reduces diffusion of nitrogen into the bulk. Initial sticking probabilities S_0 (corresponding to dissociation on the clean surface) are determined from the initial slopes of coverage vs exposure curves. Here all coverages are estimated using Auger electron spectroscopy, assuming the N-atom coverage to be proportional to the N(380 eV)/Fe(560 eV) peak-to-peak ratio.[5] Measurements are placed on an absolute scale by comparison with sticking probabilities determined by an alternative direct method based on measurement of the fraction of the beam reflected by the surface.[8,9] Beams of N_2 molecules confined to the vibrational ground state are produced by using a 300 K nozzle, varying the kinetic energy by seeding in H_2 or He. In order to produce vibrationally excited molecules, the nozzle temperature is raised to 2000 K. Here we assume that vibrational relaxation is negligible under our conditions, an assumption supported by measurements on NO beams in our system. In all cases kinetic energies are determined from flight times from a high-speed chopper to a mass spectrometer.[6–8]

The basic principle behind these measurements is similar to that described previously.[10] First the dependence of S_0 on initial kinetic energy is determined for vibrational ground state molecules using a beam source held at 300 K. Then the source is heated to 2000 K to produce beams with kinetic energies in the same range, but with substantial populations of vibrationally excited species (e.g., 80% $v = 0$, 15% $v = 1$, 3% $v = 2$, etc.). The effect of vibrational energy on dissociation is then deduced for a given kinetic energy by comparing S_0 values for the two nozzle temperatures. The curve in Fig. 1 corresponds to the function $S_0(T_{noz} = 300\ \text{K}, E)$ which is

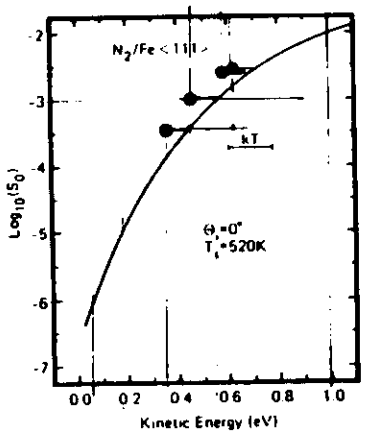


FIG. 1. Effect of kinetic energy on the initial sticking probability of N_2 on Fe(111) for beams having different vibrational temperatures. The curve corresponds to a fit to data for a 300 K nozzle while the solid circles were obtained with a nozzle heated to 2000 K and are placed according to their mean kinetic energy. The horizontal bar shows the classical vibrational energy of a diatomic molecule at 2000 K.

 0021-9606/87/130770-02$02.10

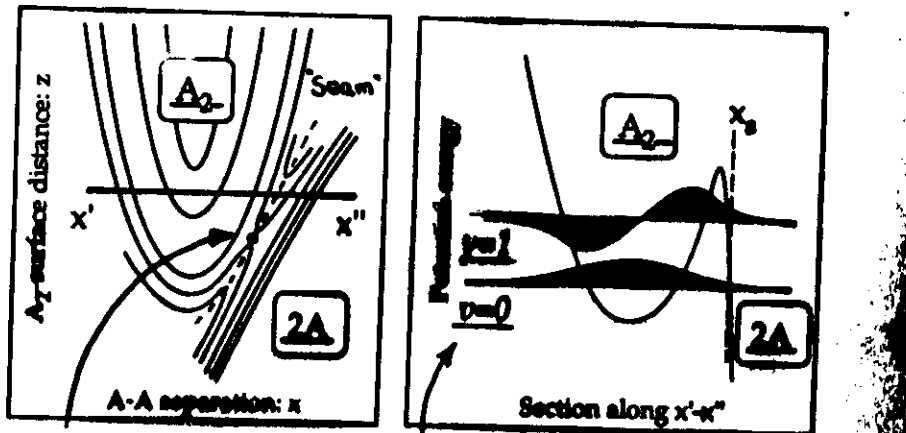
6.
5.15

Vibrationally Enhanced Dissociation

If a molecule has an internal mode excited then is it more or less reactive when encountering a metal surface?

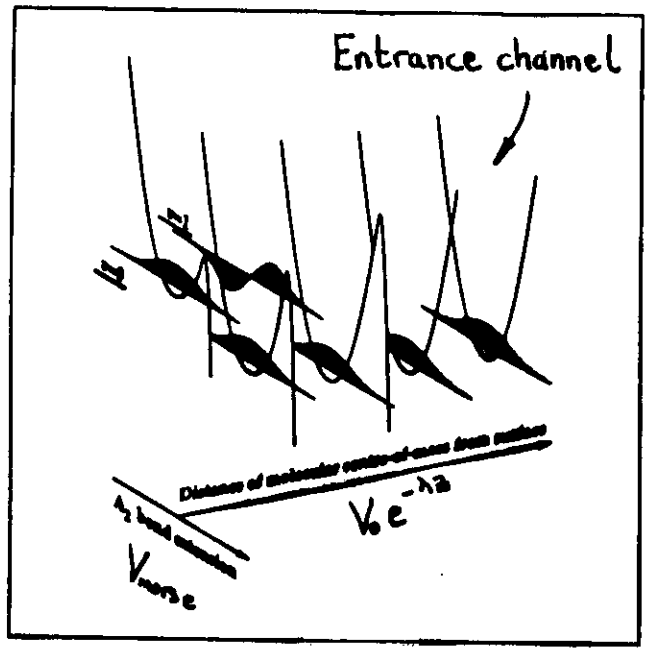
Potential energy surface

$$V(x,z) = V_{Morse} + V_o \exp(-\lambda z)$$



Transition state

Vibrational wavefunctions



Slices taken through the PES at constant values of z

Holloway, Halstead + Hodges
CPL [soon (I hope!)]

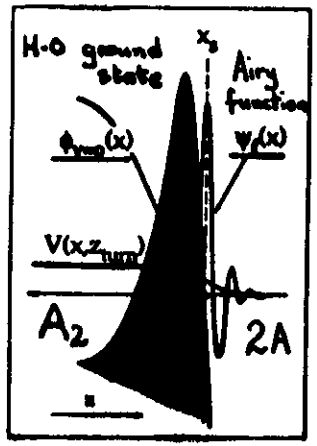
Semiclassical Scattering

Model

"Mass" in the x-direction = $0.5m_{atom}$ (red. mass μ)
"Mass" in the z-direction = $2.0m_{atom}$

Treating the motion in z classically and that in x quantum mechanically, it is clear that for a given translational energy, a classical turning point in "z" is achieved. Using the Golden rule expression for the tunneling rate from an initial vibrational state $\phi_v(x)$ to a range of final states $\psi_f(x)$

$$R \sim CV^2/\Delta E \sum_f |\langle \phi_v | \psi_f \rangle|^2$$



The final state ψ_f may be well approximated by

$$\psi_f \sim \sqrt{m/(v+0.5)}\ \delta(x-x_s)$$

R.L. Sundberg and E.J. Heller, J. Chem. Phys. 80, 3600 (1984).

Giving

round trip time $\sim \frac{1}{\sqrt{E_v}}$

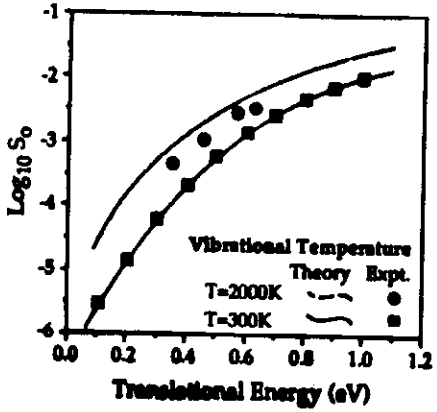
$$S(v,x_s) \sim \sqrt{m/E_v(v+0.5)}\ |\phi_v(x_s)|^2$$

Results

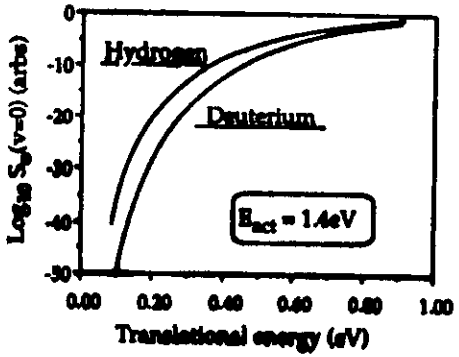
N_2/Fe(111)

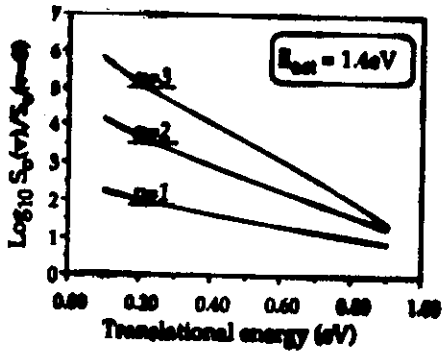
Ground-state data fitted to obtain $X_3(Z_{turn})$.

$$S(T) = \sum_v S_v e^{-E_v/kT}$$

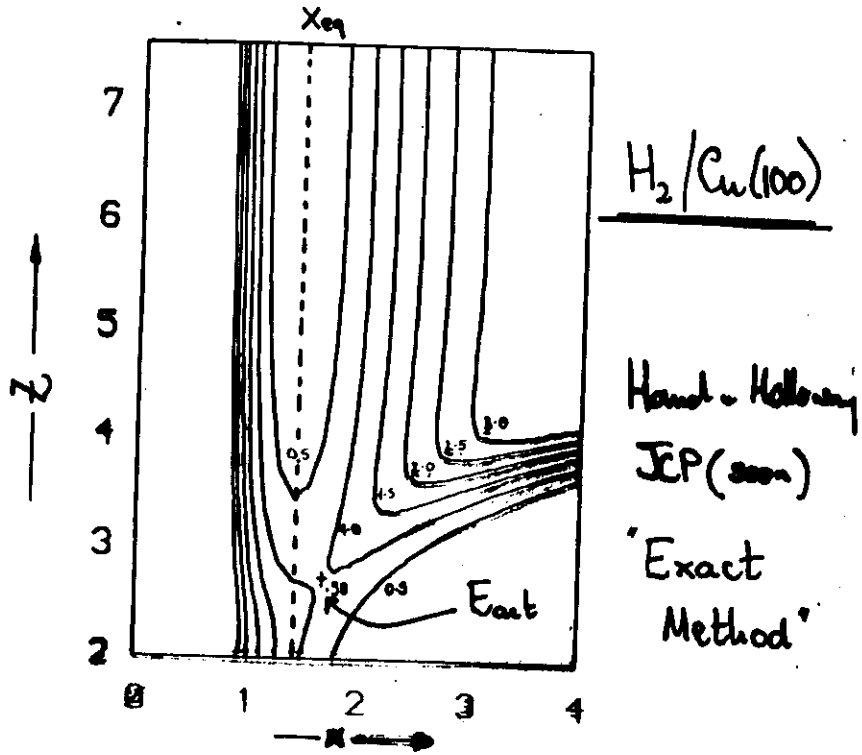


H_2/Cu(100) (prediction!)





Holloway, Hodgson, Halstead J. Chem Spect 45 [illegible]



H_2/Cu(100)

Hand-Holloway JCP (soon)

"Exact Method"

Sticking Coefficient

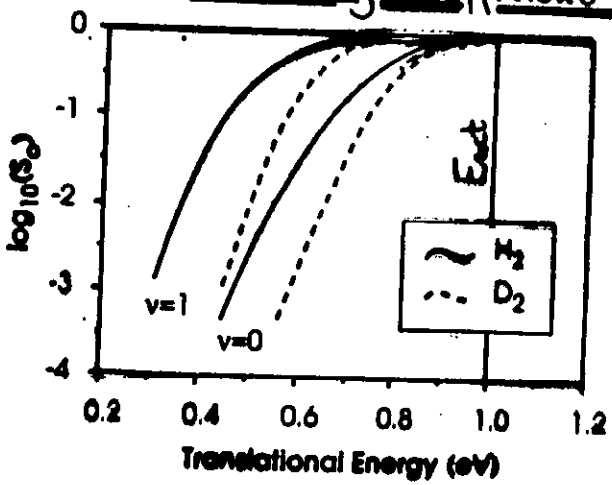


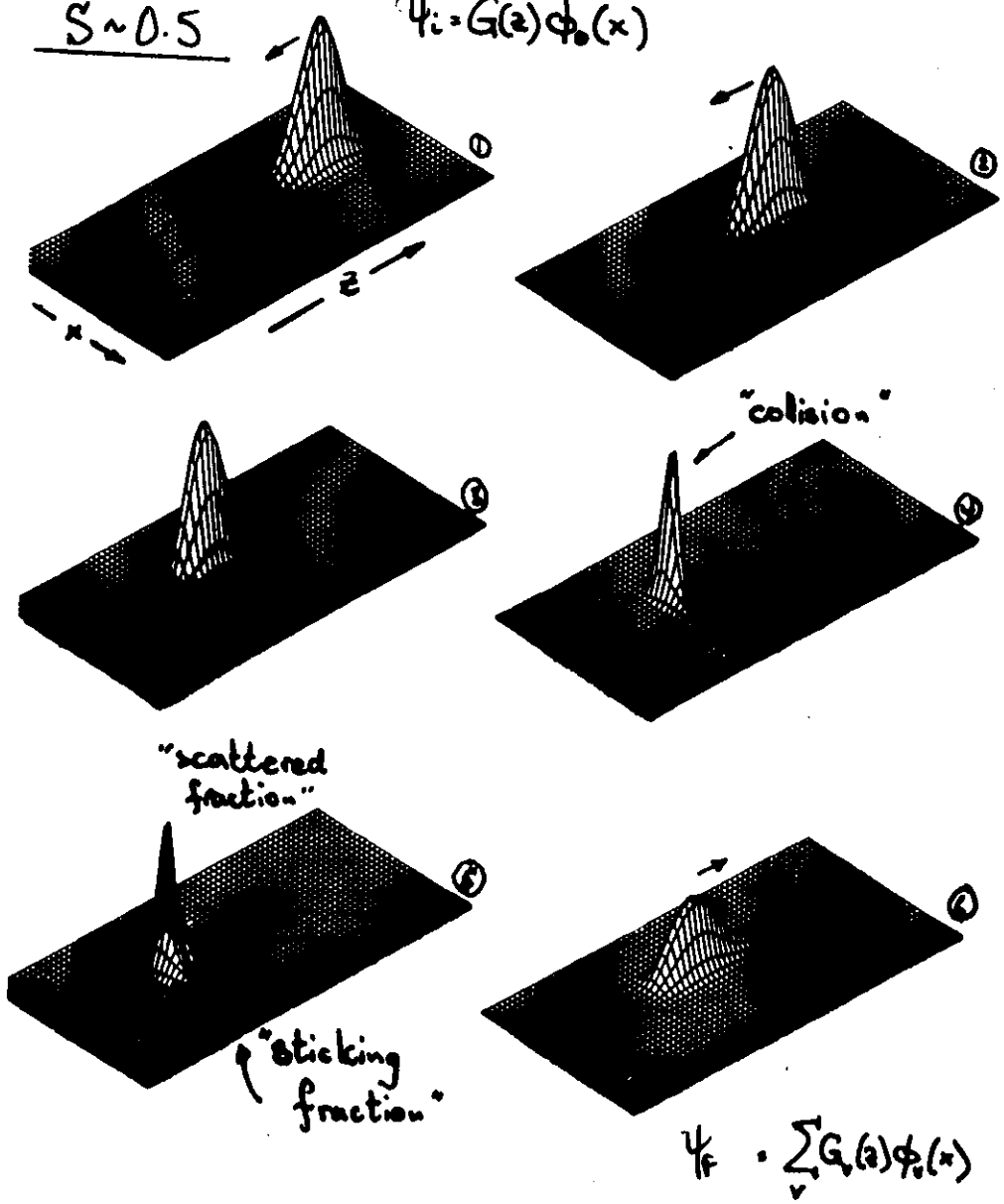
Figure 1

Time-evolution of wavepacket on a "sticking-trajectory"

$E_i = 1.05 eV$

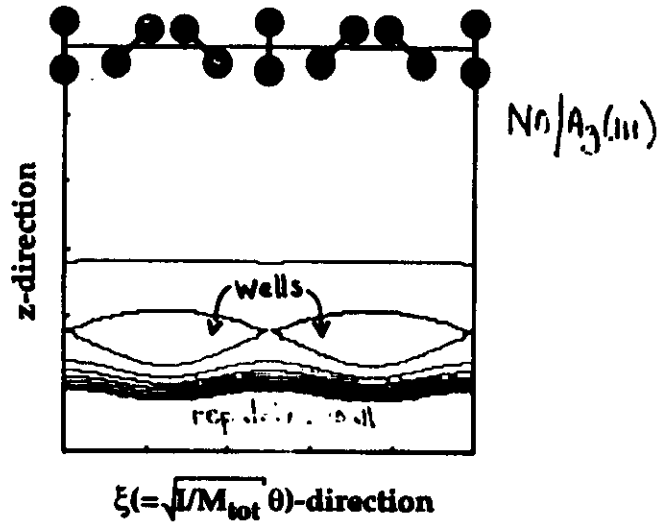
$S \sim 0.5$

$\Psi_i = G(z)\phi_0(x)$



$\Psi_f = \sum_v G_v(z)\phi_v(x)$

A Time-Dependent Formalism for *Rotational* Scattering



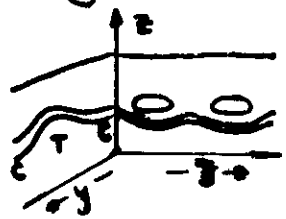
→ Diagonalize the KE operator

→ Use the semiclassical gaussian propagator to develop the wavefunction in time $\Psi_i = e^{-ikz}$

→ Project out the final angular momentum states "J" $\Psi_f \sim \sum_J S_J e^{ik_J \beta}$

Comments.

- Homonuclear molecule reduces ξ periodicity ($0<\theta<\pi$) → $J_{n\to n+2}$
- H_2/HD ? different PES because of c.of m. shift → increased S_J → $J_{n\to n+1}$
- Vary initial J by providing (quantized) momentum in $\mathcal{Y}$ → rotational pumping
- Include surface periodicity → corrugation + activation barriers



- Aligned molecules → for J=0 span a part of $\mathcal{Y}$ space
- Phonon coupling → either by driven oscillator (Brenig) or by multidimensional gaussians (Drolshagen + Heller)

CONCLUSIONS

- ➤ *Basic level of understanding*
- ➤ *Multi-dimensional approach*
- ➤ *Isolate important features*
  - *adsorbate modes*
  - *substrate modes*
  - *unit-cell morphology*
- ➤ *Classical/Quantum mechanics*
- ➤ *New, state-resolved experiments are vital*