Gas Surface Interactions

As a molecule approaches a surface the molecule can/will undergo:

Momentum exchange,
Energy exchange, between internal degrees of freedom
(translational, rotational, vibrational, or electronic)
or to /from the surface.

These in turn lead to various known *observable phenomema* including;

Elastic scattering:
Reflection,

Diffraction.

Inelastic scattering:
Single phonon annihilation/creation
Multi-phonon scattering
e^-- hole pair creation

Rotational rainbows

Temporary trapping
Bound state resonances
Mobile precursor states

Long-term trapping
Physisorption
Molecular chemisorption
Dissociative chemisorption

Electron transfer:
Molecular ion adsorption
Molecular ion desorption
Electron emission
DIET processes.

Increasing Gas-Surface Interaction

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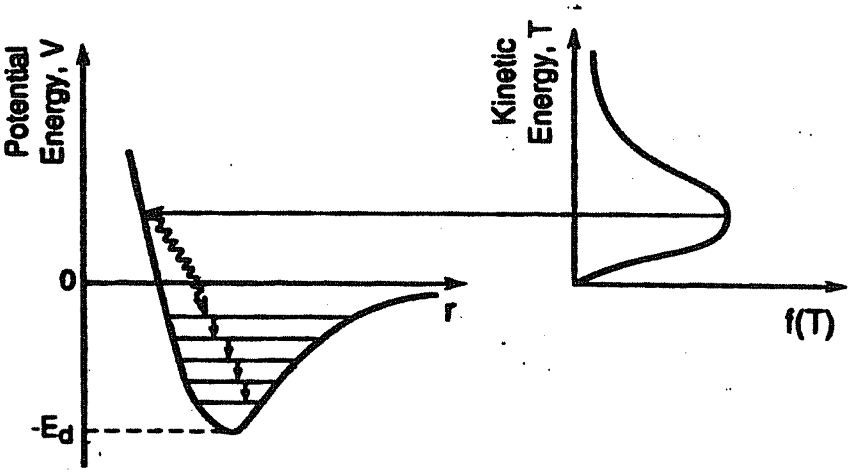
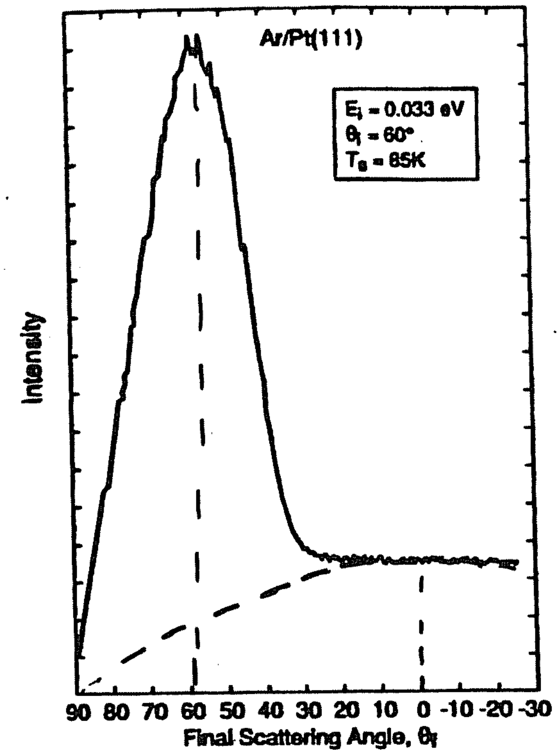


Figure 5 *Illustration of the trapping mechanism of gas-phase atoms or molecules [represented by the Maxwell–Boltzmann distribution of kinetic energies,* f(T)*] at a surface via inelastic interactions with the repulsive part of the surface potential (curve shown on the left)*



INCREASING LOSS RATIO $\frac{\Delta E_\perp}{\Delta E_\parallel}$ ←

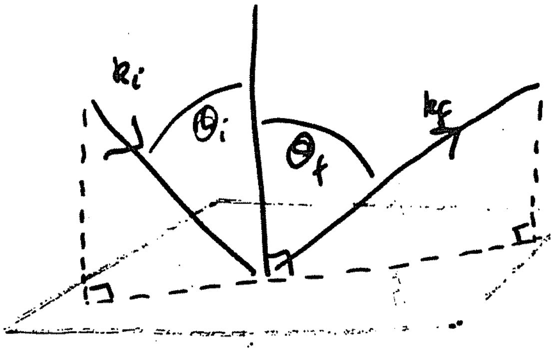
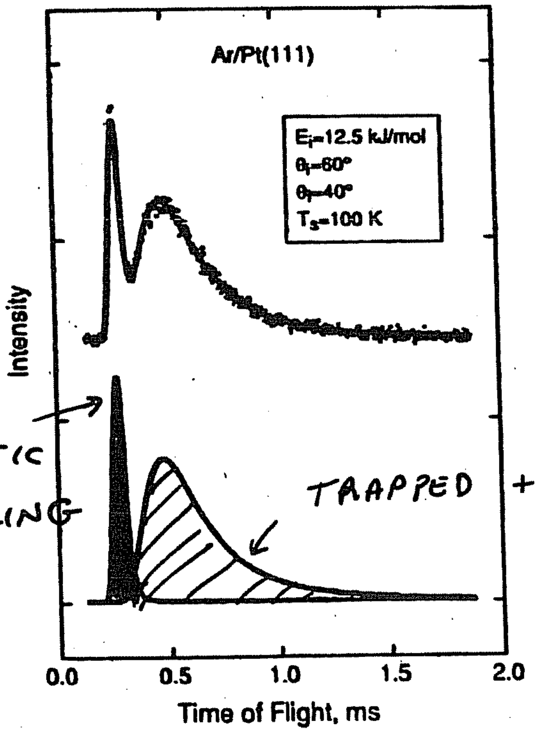


Figure 6 *Scattering distribution of* Ar *from the* Pt(111) *surface as a function of the final scattering angle, θ_f, at a surface temperature of* 85 K
(Reproduced with permission from reference 88)



DIRECT INELASTIC SCATTERING

TRAPPED + DESORBED

Figure 7 *Time-of-flight spectra of scattered* Ar *from the* Pt(111) *surface at a surface temperature of* 100 K. *The upper curve represents the experimental data, and the bottom curves represent the deconvolution of these data into a 'direct-inelastic' scattering component (sharp peak, high energy) and a 'trapping-desorption' scattering component (diffuse peak, lower energy)*
(Reproduced with permission from reference 88)

Energy Accommodation

in temporarily trapped species

Accommodation Coefficient, α,

$$\alpha = \frac{< E_{des} > - E_i}{k_B T_{surf} - E_i}$$

Two extreme cases;

1) $\alpha = 0$ as $<E_{des}> = E_i$

Trapping does not occur.

2) $\alpha = 1$ as $<E_{des}> = k_B T_{surf}$

Complete thermal equilibration with the surface, long-term trapping occurred.

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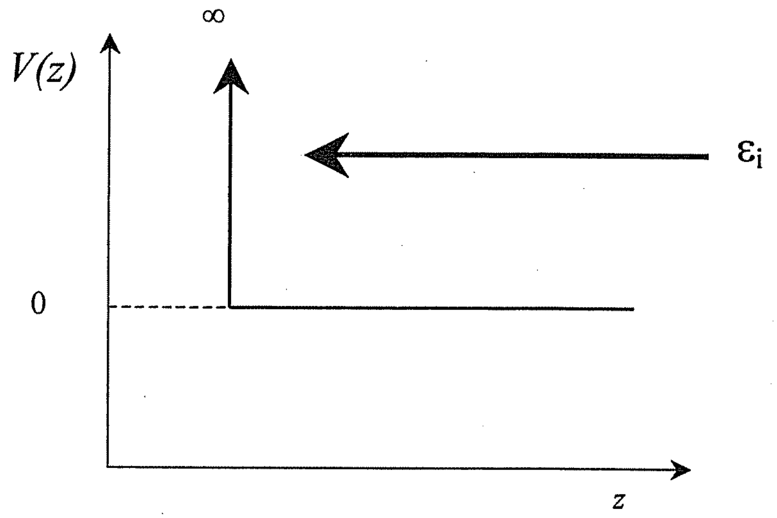
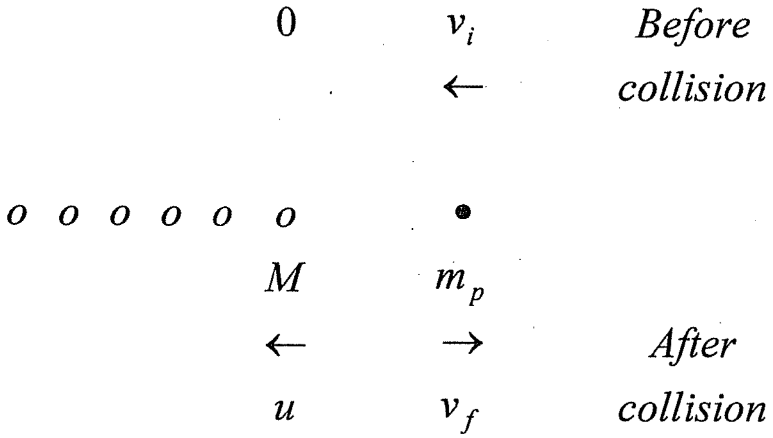
Baule Formula

Fast Collisions, 1-D model for energy transfer, leading to trapping



Think of



Conservation of Energy;

$$\varepsilon_i = \frac{1}{2} m_p v_i^2 = \frac{1}{2} m_p v_f^2 + \frac{1}{2} M u^2$$

Conservation of (1-D) Momentum;

$$m_p v_i = M u - m_p v_f$$

Eliminate v_f :

$$m_p v_i^{\,2} = m_p \left(\frac{m_p v_i - M u}{m_p} \right)^2 + M u^2$$

$$v_i^{\,2} = v_i^{\,2} - 2\frac{v_i M u}{m_p} + \frac{M^2 u^2}{m_p^{\,2}} + \frac{M u^2}{m_p}$$

$$2 v_i \frac{M}{m_p} = \left(\frac{M^2}{m_p^{\,2}} + \frac{M}{m_p} \right) u$$

$$2 v_i = \left(\frac{M}{m_p} + 1 \right) u$$

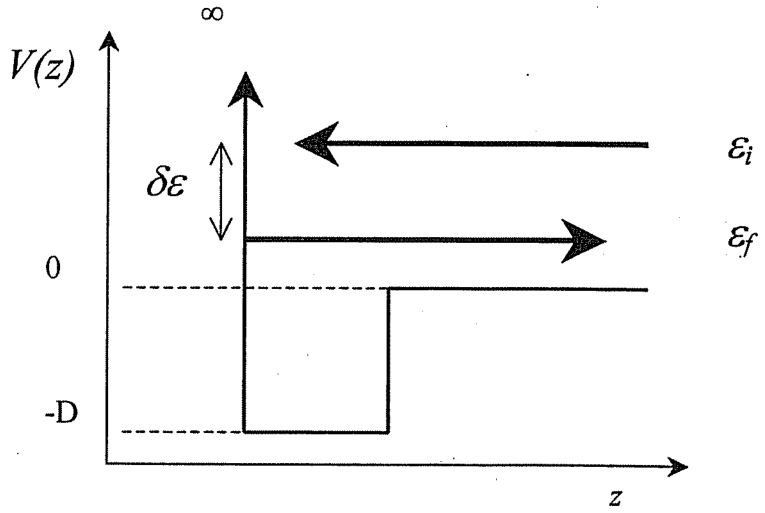
Energy transferred to surface atom, δε,

$$\delta\varepsilon = \frac{1}{2} M u^2 = \frac{M}{2} 2^2 v_i^{\,2} \left(\frac{1}{\mu} + 1 \right)^{-2} = \frac{2\mu}{(1+\mu)^2} m_p v_i^{\,2}$$

$$= \frac{4\mu}{(1+\mu)^2}\, \varepsilon_i$$

$$\mu = \frac{m_p}{M}$$

Same model with modified potential, with potential well....



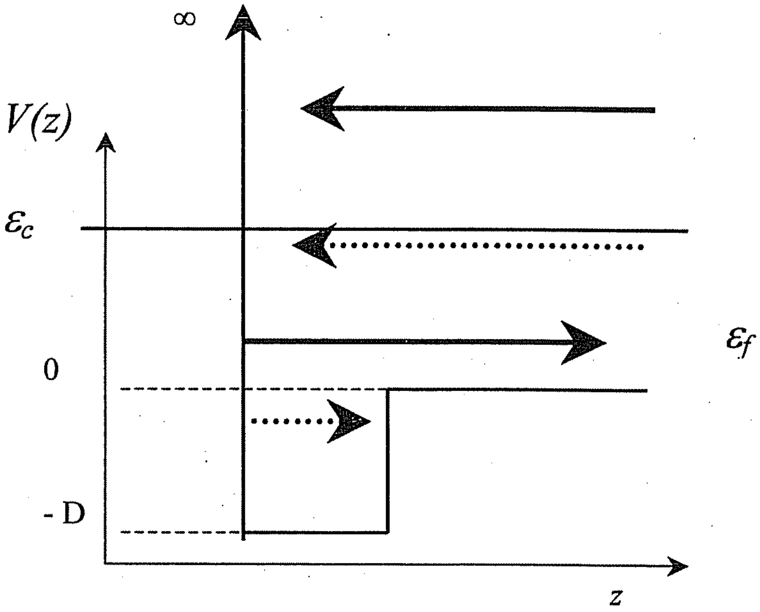
$$\delta\varepsilon = \frac{4\mu}{(1+\mu)^2}(\varepsilon_i + D) \quad .$$

When does trapping occur?

Answer, when $\delta\varepsilon > \varepsilon_i$. .

I.e. when $\varepsilon_i < \varepsilon_c$

where $\varepsilon_c = \dfrac{4\mu D}{(1-\mu)^2}$.



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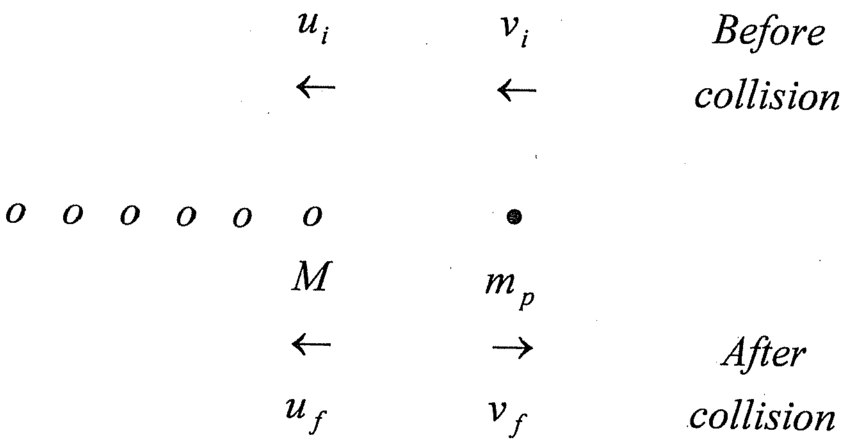
Consider limitations of that model;

1) Finite surface temperature.

Fast collisions again.



$$\delta\varepsilon = \frac{4\mu\left(\varepsilon_i - \frac{1}{2}M u_i^{\,2}\right) + 2m_p v_i(1+\mu)u_i}{(1+\mu)^2}$$

$$\Rightarrow \quad <\delta\varepsilon(T_s)> \;\approx\; \frac{4\mu(\varepsilon_i - k_B T)}{(1+\mu)^2}$$

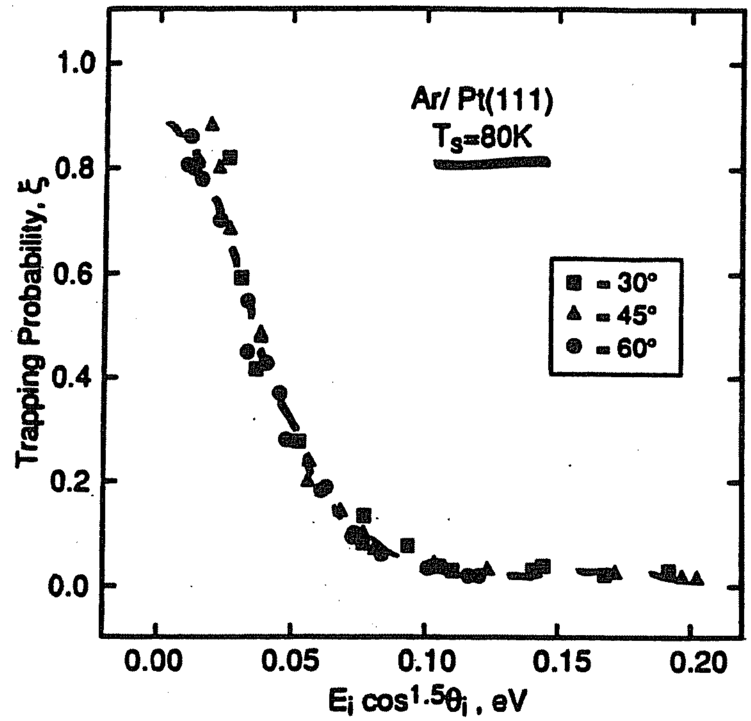
Energy accommodation coefficient, α,

$$\alpha = \frac{\varepsilon_i - <\varepsilon_f>}{\varepsilon_i - k_B T} = \frac{<\delta\varepsilon>}{\varepsilon_i - k_B T}$$

Our model gives

$$\alpha = \frac{4\mu}{(1+\mu)^2} \quad .$$

I.e. the energy accommodation coefficient depends only on the incoming and surface masses!

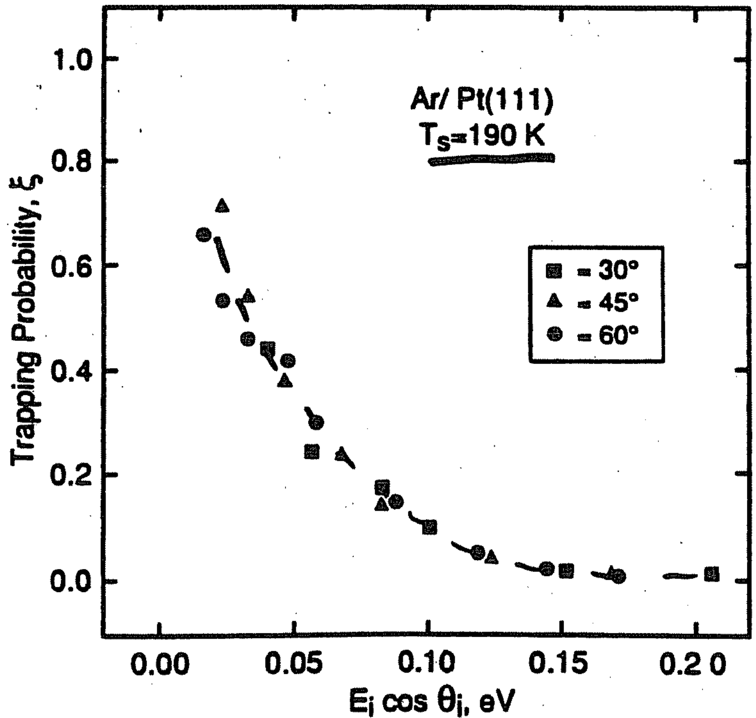


Universal curve,

Exponent $n = 1.5$

$E_i \cos^{1.5} \theta_i$

Figure 10 *Trapping probability of* Ar *on* Pt(111) *as a function of* $E_i \cos^{1.5}\theta_i$ *at a surface temperature of* 80 K
(Reproduced with permission from *Chem. Phys. Lett.*, 1989, **163**, 111)

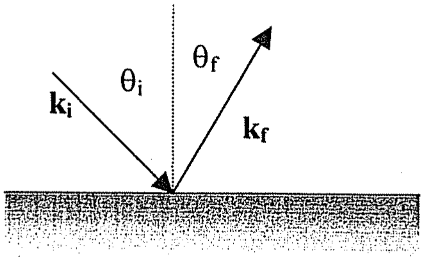


$n = 1.$

Figure 11 *Trapping probability of* Ar *on* Pt(111) *as a function of* $E_i \cos\theta_i$ *at a surface temperature of* 190 K
(Reproduced with permission from *Chem. Phys. Lett.*, 1989, **163**, 111)

2) Multi-dimensional surfaces!

The definition of trapping is that $\varepsilon_i^z \rightarrow \varepsilon_f^z < 0$ (Bound State)
But incident particle is characterized by parallel and perpendicular energies, ε_i^{ll} and ε_i^z respectively.



$k_i = (K_i, k_i^z) = K_i^x x + K_i^y y + k_i^z z$

$\varepsilon_i^{ll} = h^2|k_i|^2 \sin^2\theta_i / 8\pi^2 m$

and $\varepsilon_i^z = h^2|k_i|^2 \cos^2\theta_i / 8\pi^2 m$.

$(\varepsilon_i^{ll} + \varepsilon_i^z = \varepsilon_i)$

Trapping probability, ξ, can be anywhere between two extremes:

A) $\xi = f(\varepsilon_i^z)$ alone

Normal Energy Scaling

B) $\xi = f(\varepsilon_i)$ alone

Total Energy Scaling

The prevalence of Case A or B is determined by the surface roughness, periodicities, and/or ease of parallel to perpendicular momentum transfer.

Generally, rough surfaces can aid in sticking/trapping.
(That can be thermally induced, or static roughness.)

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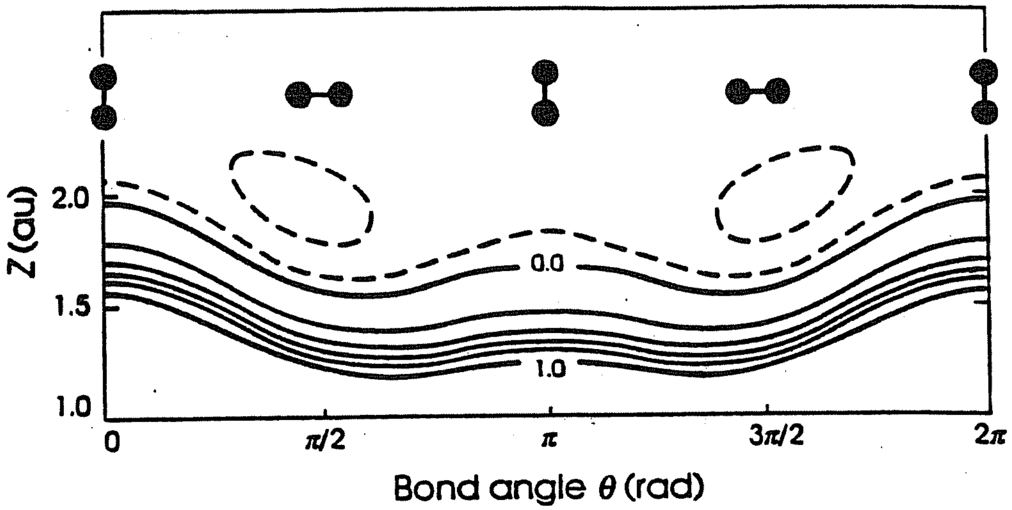
DIATOMIC MOLECULAR ORIENTATIONS.



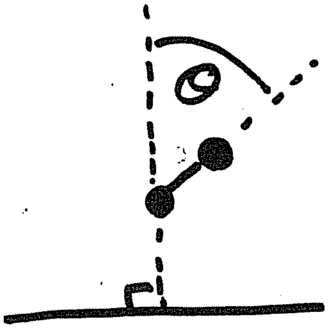


Figure 2 *A contour plot of the Voges–Schinke potential energy surface*[47] [*equation (28)*] *for the two-dimensional model of* NO *interacting with* Ag(111) *described in the text. The* Z *direction measures the distance of the molecular centre-of-mass above the surface and θ the angle between the* NO *bond and the surface normal. The energies shown are in* eV

$$V = V_R + V_{VdW}$$

$$V_R = V_{R00}\, e^{-\gamma z} \left\{ 1 + \alpha_R P_1(\cos\theta) + \beta_R P_2(\cos\theta) \right\}$$

$$V_{VdW} = \frac{C_{VdW}}{|z - z_{VdW}|^3} \left\{ 1 + \alpha_{VW} P_1(\cos\theta) + \beta_{VW} P_2(\cos\theta) \right\}$$

ROTATIONAL RAINBOWS

Gradient gives T_{rot}.

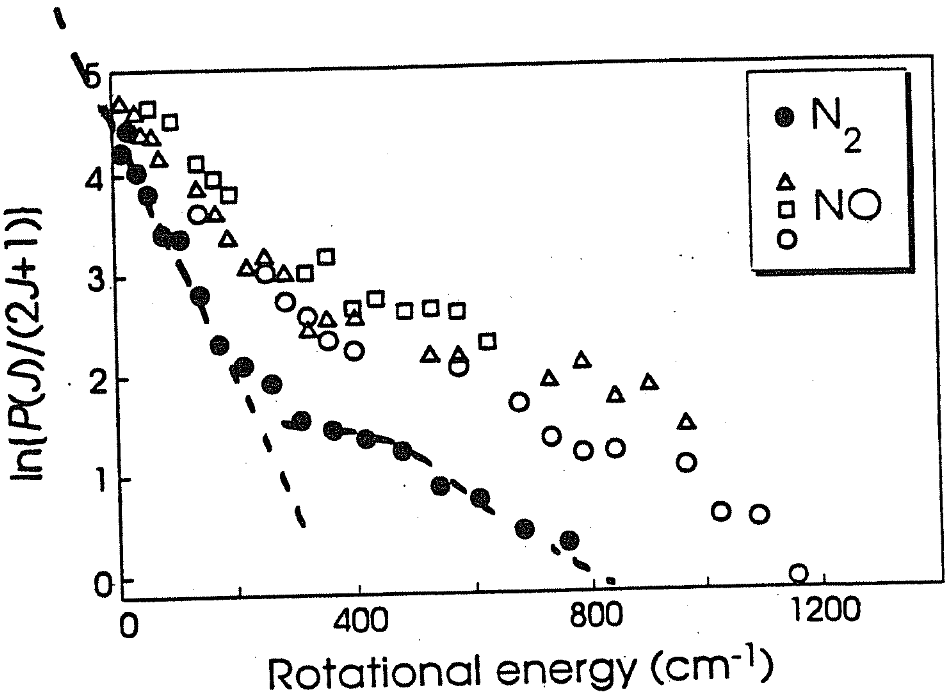
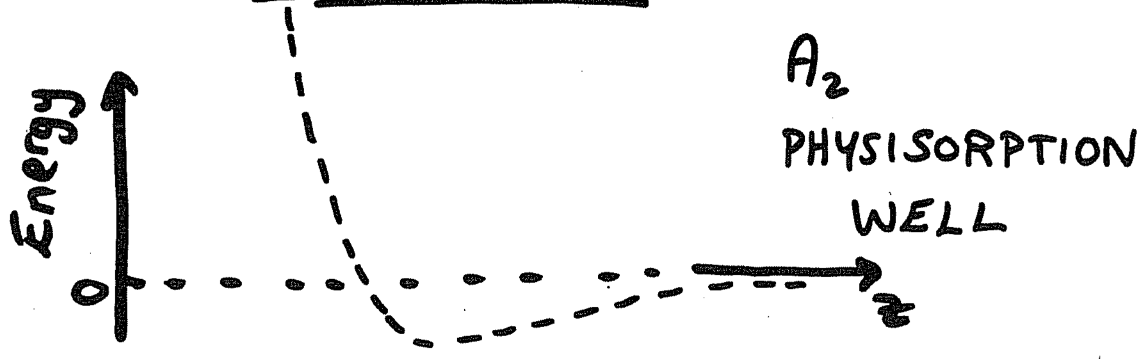
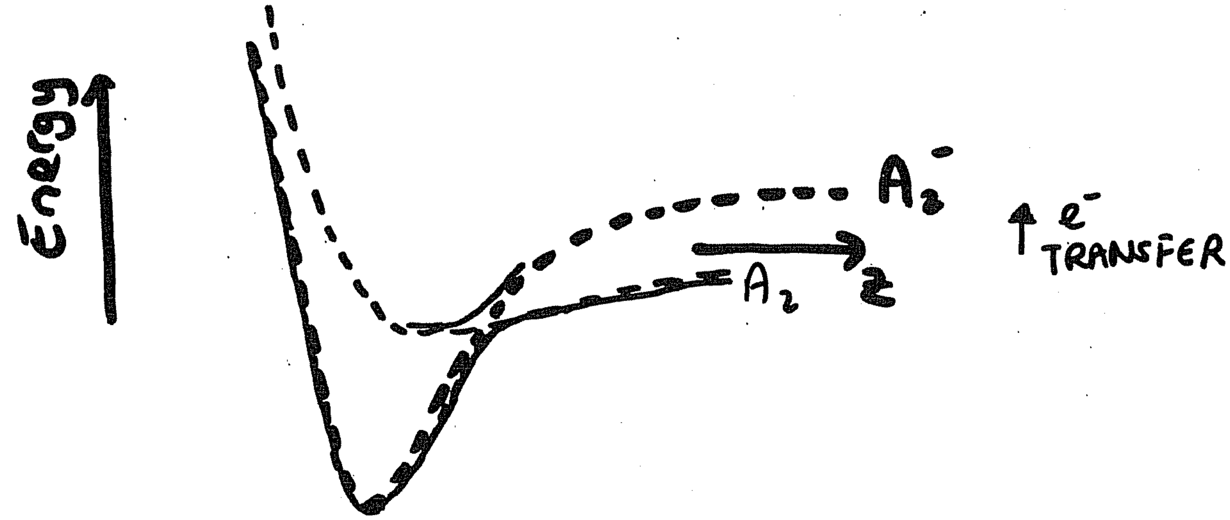


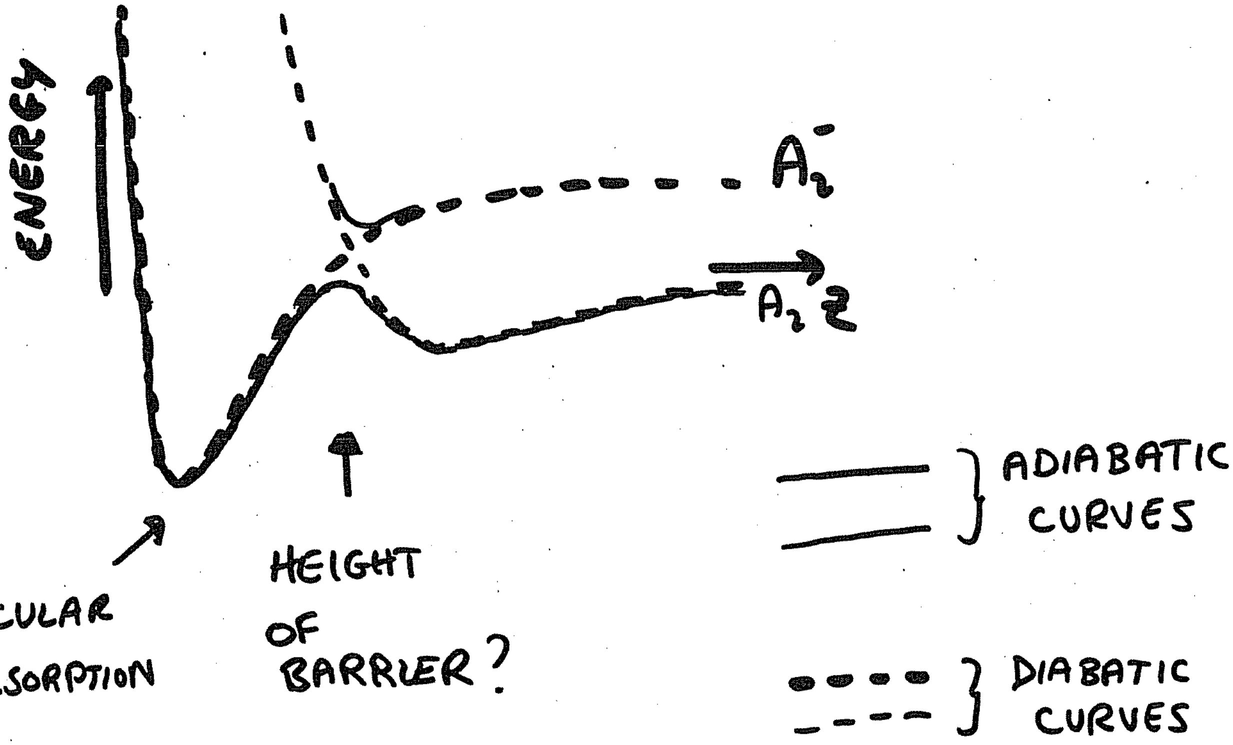
Figure 8 *Comparison of Boltzmann plots for* N_2 *and* NO *scattered from* Ag(111) *under similar conditions*[30]

N_2, NO rotationally cold; backscattered from Ag(111)

ELECTRON TRANSFER + CHEMISORPTION







MOLECULAR CHEMISORPTION

HEIGHT OF BARRIER?

ACTIVATED CHEMISORPTION?

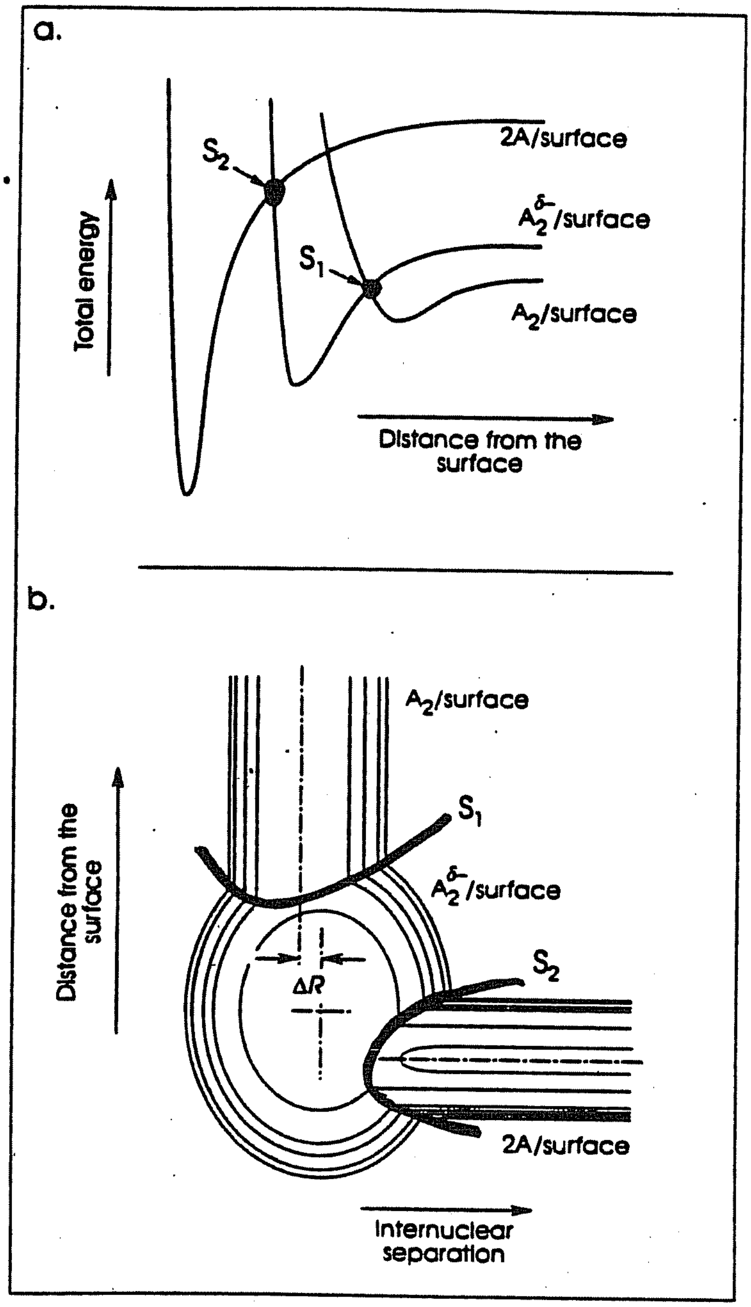


Figure 9 (a) *A more general form of Figure 1 where the presence of a third electronic state, corresponding to a negative molecular ion, is interposed between the molecular and chemisorption diabatic states. Depending upon the relative position of the states, an activation barrier can occur at one of two places,* S_1 *or* S_2. (b) *A contour plot for the lowest energy diabatic states where both the molecule–surface distance and the molecular bond length have been included. The geometry corresponds to a molecule approaching with its axis parallel to the surface ('elbow plot').* S_1 *and* S_2 *now appear as crossing seams rather than unique points in space*[20]

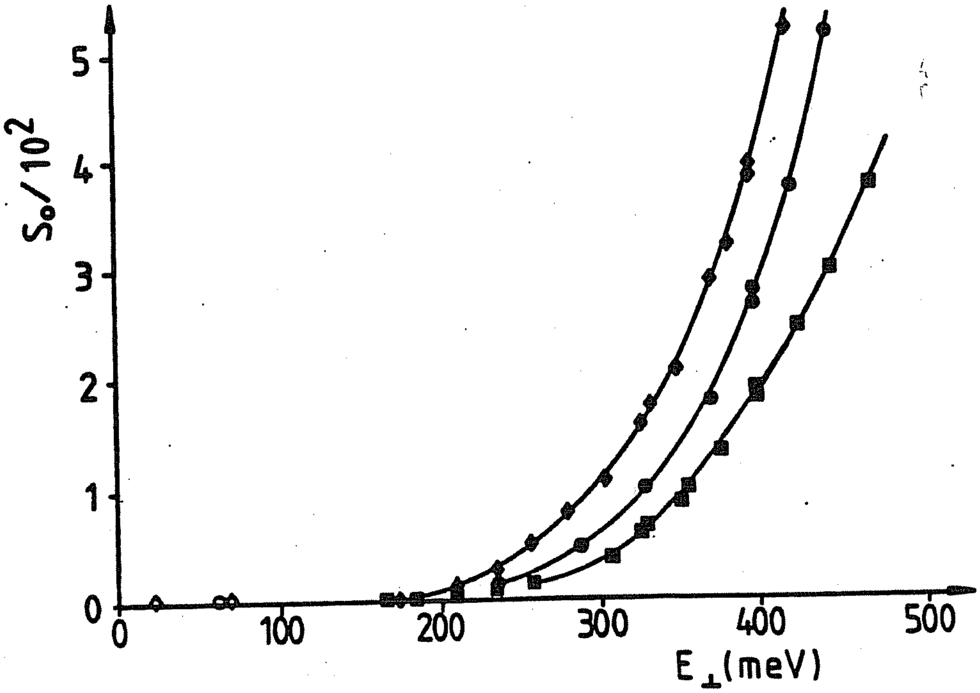
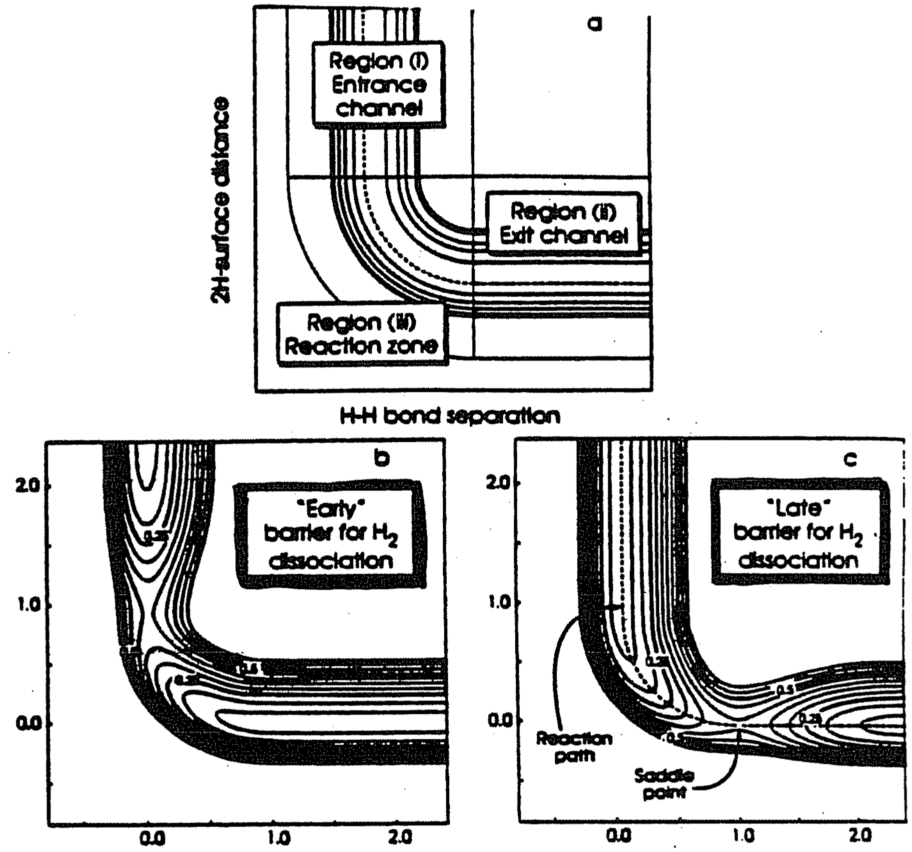


Figure 10 *The initial sticking probability* S_0 *of* H_2 *as a function of* $E_\perp$ *on* Cu(111) (◆), Cu(100) (●) *and* Cu(110) (■).[27] T_s = 100 K

ACTIVATED ADSORPTION

$E_a \gtrsim 450$ meV.

H_2 on Cu again!



?

Figure 13 (a) *A contour diagram showing the essential features of this model potential energy surface. This template is then combined with a Gaussian barrier whose potential is varied in order to create surfaces with two different topologies.* (b) *Here the maximum of the dissociation barrier lies at the beginning of the reaction zone—an early barrier.* (c) *The activation barrier maximum is placed at the beginning of the exit channel—a late barrier. In this figure is shown the reaction path defined by equation (40). Energies are in* eV *and are measured with respect to a molecule infinitely far from the surface*[23]

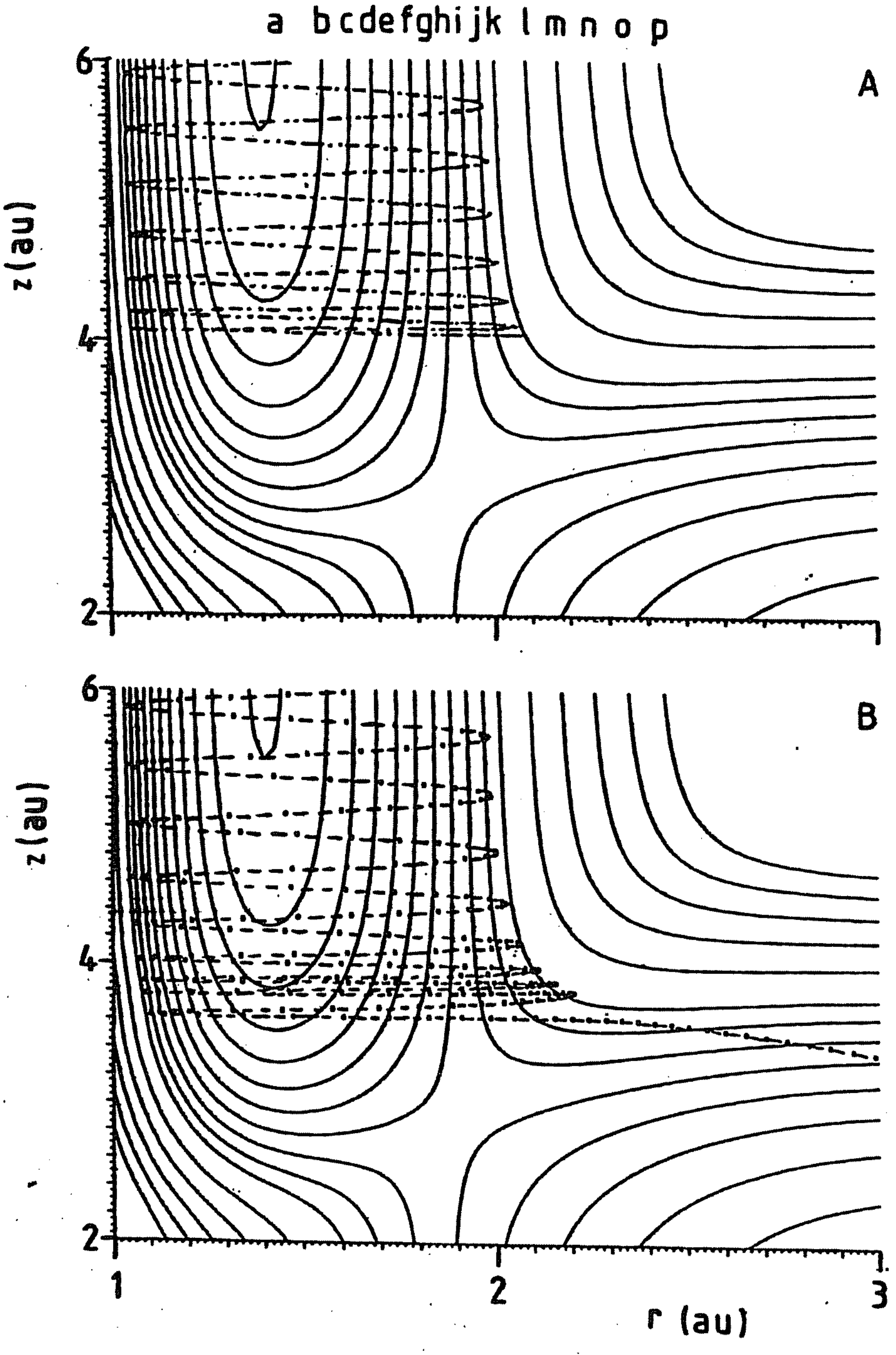


Figure 15 *The classical trajectories over a 2D-PES*[26] *illustrating the effect of vibrational adiabaticity (or 'bootstrapping') in the entrance channel. The trajectories are for* $D_2(v = 2)$ *over a potential where the saddle point energy is at* 720 meV. *An initial value* $E_\perp = 50$ meV *leads to an 'in and out' trajectory* (A), *while for* $E_\perp = 63$ meV *dissociation takes place* (B). *The potential energy contours (in* eV*) are* a = 0, b = 0.1, c = 0.2, d = 0.3, e = 0.4, f = 0.5, g = 0.6, h = 0.7, i = 0.8, j = 0.9, k = 1.0, l = 1.2, m = 1.4, n = 1.6, o = 1.8, p = 2.0

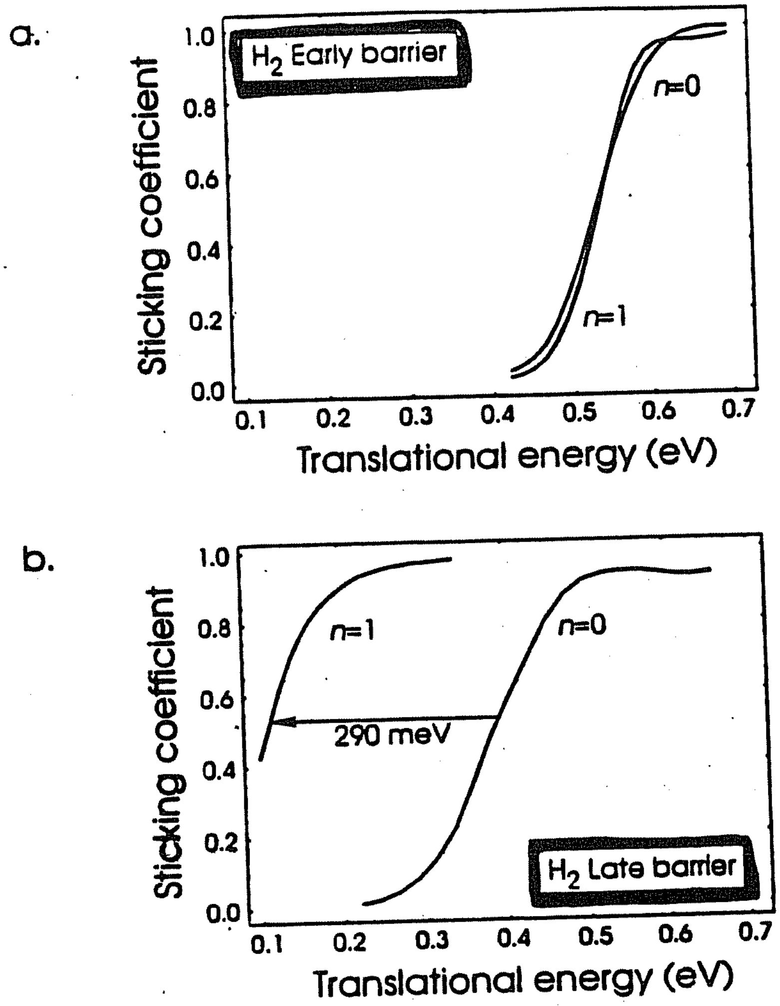


Figure 15 *A comparison of the dissociation probability for a* H_2 *molecule in its ground and first vibrationally excited state.* (a) *Shows the results for the early barrier PES and indicates that there is a minimal effect resulting from the additional vibrational energy.* (b) *In this late barrier case, where the barrier lies wholly in the vibrational co-ordinate (bond extension of* 1.0 a.u.*), the shift of* 290 meV *still only represents a usage of 56% of the available vibrational energy. For both potentials, it is found that the de-excitation probability for vibrationally excited molecules is* < 10%*, lending weight to the concept of vibrational adiabaticity in the scattering dynamics*[23]

H_2 / Cu(111)

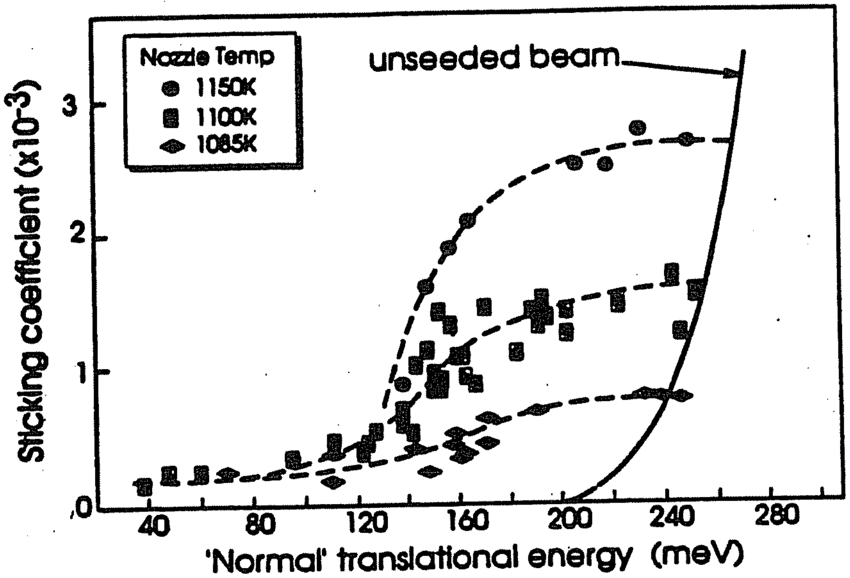


Figure 16 *The experimental results for the sticking of a pure beam of* H_2 *molecules (thick solid line). In this experiment, translational and vibrational energy change together, making it impossible to separate their individual effects on dissociation.*[77] *The calculated Boltzmann population of the* n = 1 *state is more than sufficient to account for the observed sticking.*[79] *To investigate the efficiency of vibrational energy, the nozzle is held at a fixed temperature, thereby maintaining the Boltzmann population. The translational energy is then decreased by anti-seeding with* He. *The independence of the sticking coefficient for normal translational energies greater than* 160 meV, *can be accounted for by assuming a saturation in the* n = 1 *dissociation probability (see Figure 15b)*

↑ increasing nozzle temperat

↓ decreasing nozzle temperature

←

increased proportion of heavier atoms. (He)