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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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SMR. 628 - 17

Research Workshop in Condensed Matter, Atomic and Molecular Physics
(22 June - 11 September 1992)

Working Party on:
"Energy Transfer in Interactions with Surfaces and Adsorbates"
(31 August - 11 September 1992)

"The Role of Adsorbate Degrees of Freedom in Sticking" (Part II)

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Role of adsorbate degrees of freedom in sticking.

Because of large energy separation of rotations and vibrations they can to 1st order be treated separately:

1) Rotations (rotational cooling)

Coworkers:

Kasai, Brümmer, Haug

Experiments: Various

2) Vibrations (vibrational heating)

Coworkers:

Kasai, Küchenhoff, Chiba

Experiments:

Kubiak, Zare H_2, D_2/Cu (Desorption)

Rendulic " /Cu (Sticking)

Zacharias et al. H_2, HD, D_2 /Pd (Desorption)

ϑ - distribution NO/Pt ; 0.08 eV

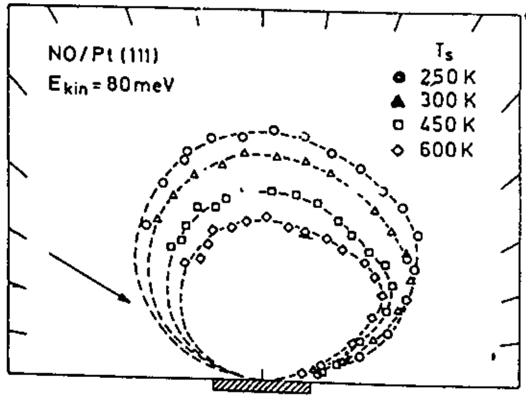


Fig. 3. Angular distributions of NO molecules scattered from a Pt(111) surface at different surface temperatures for E_{kin} = 80 meV and an incidence angle of 60°.

ε_j - distribution

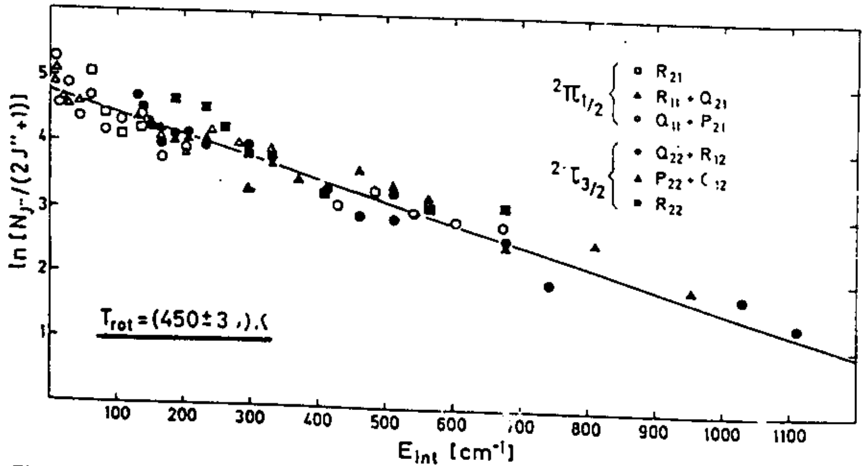


Fig. 4. Rotational state distribution for NO molecules scattered from a Pt(111) surface at 890 K. The straight line represents a Boltzmann distribution fitted to the measured points. Rotational populations of the two electronic ground states are superimposed in the diagram (E_{int} = internal energy).

Segner, ..., Häger, ..., Walther (Surf. Sci 131 273 ('83)

DAVID S. KING AND RICHARD R. CAVANAGH

Adv. Chem. Phys. LXXVI, 45 ('89)

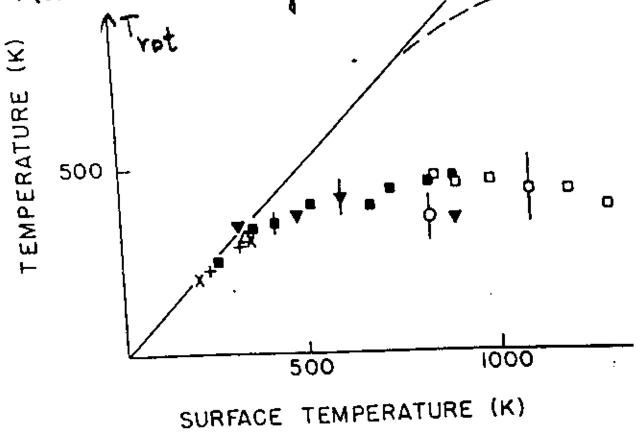
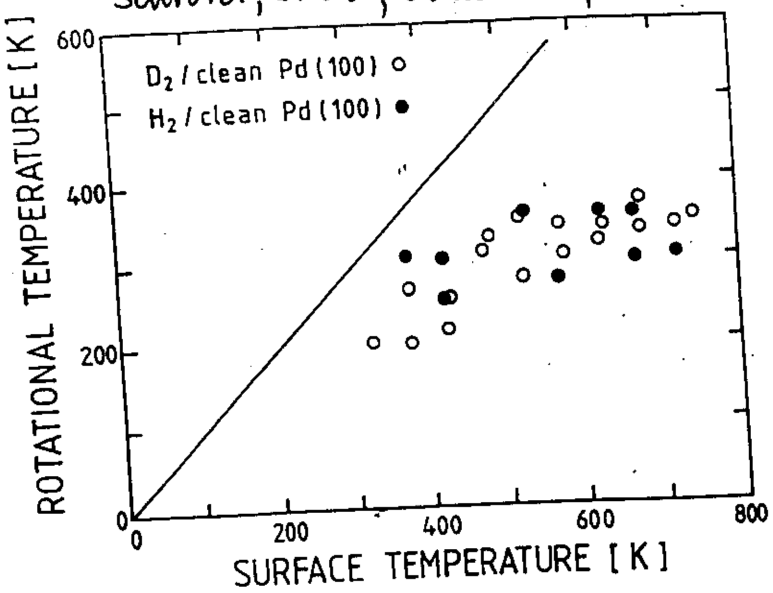
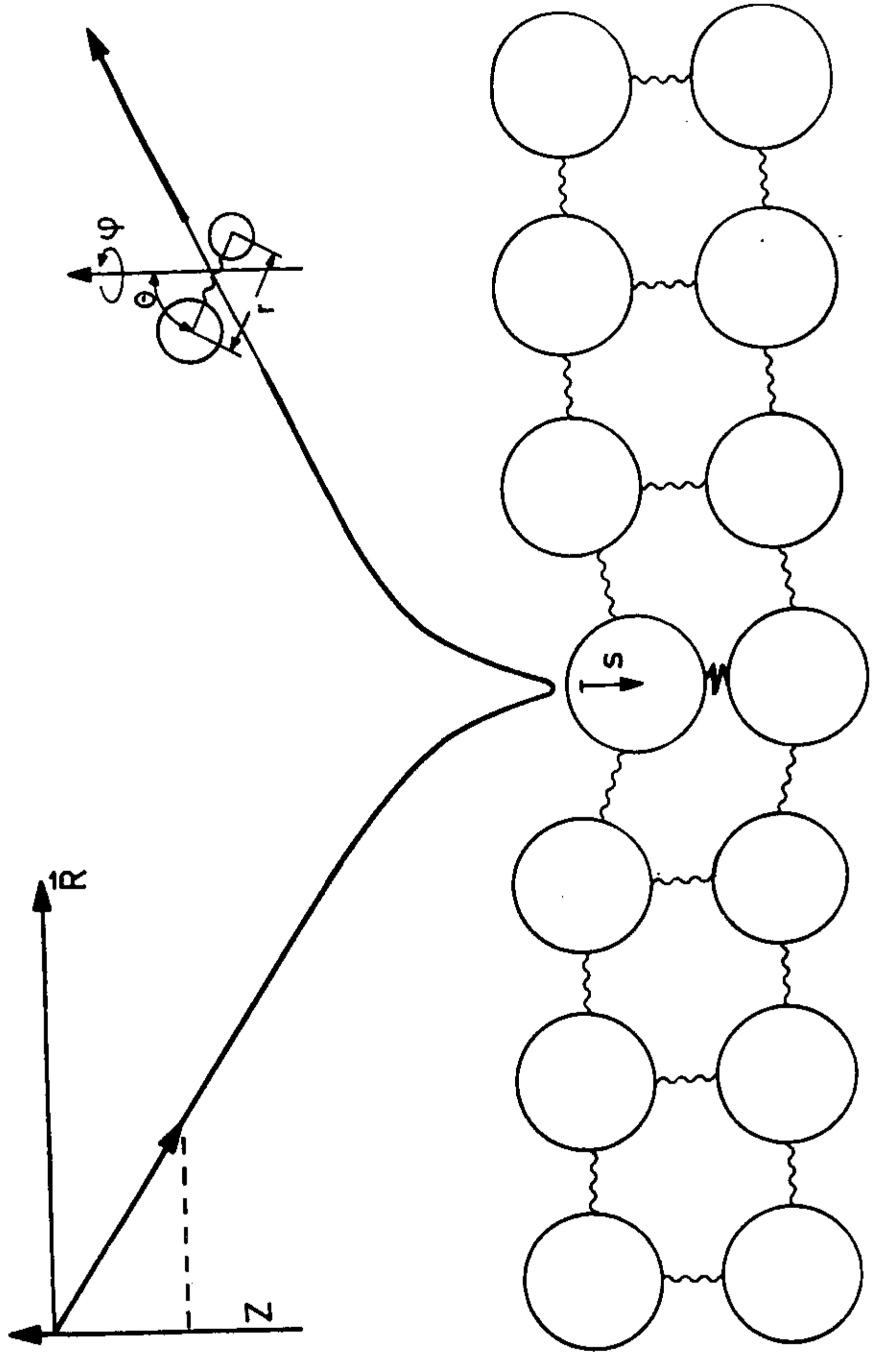
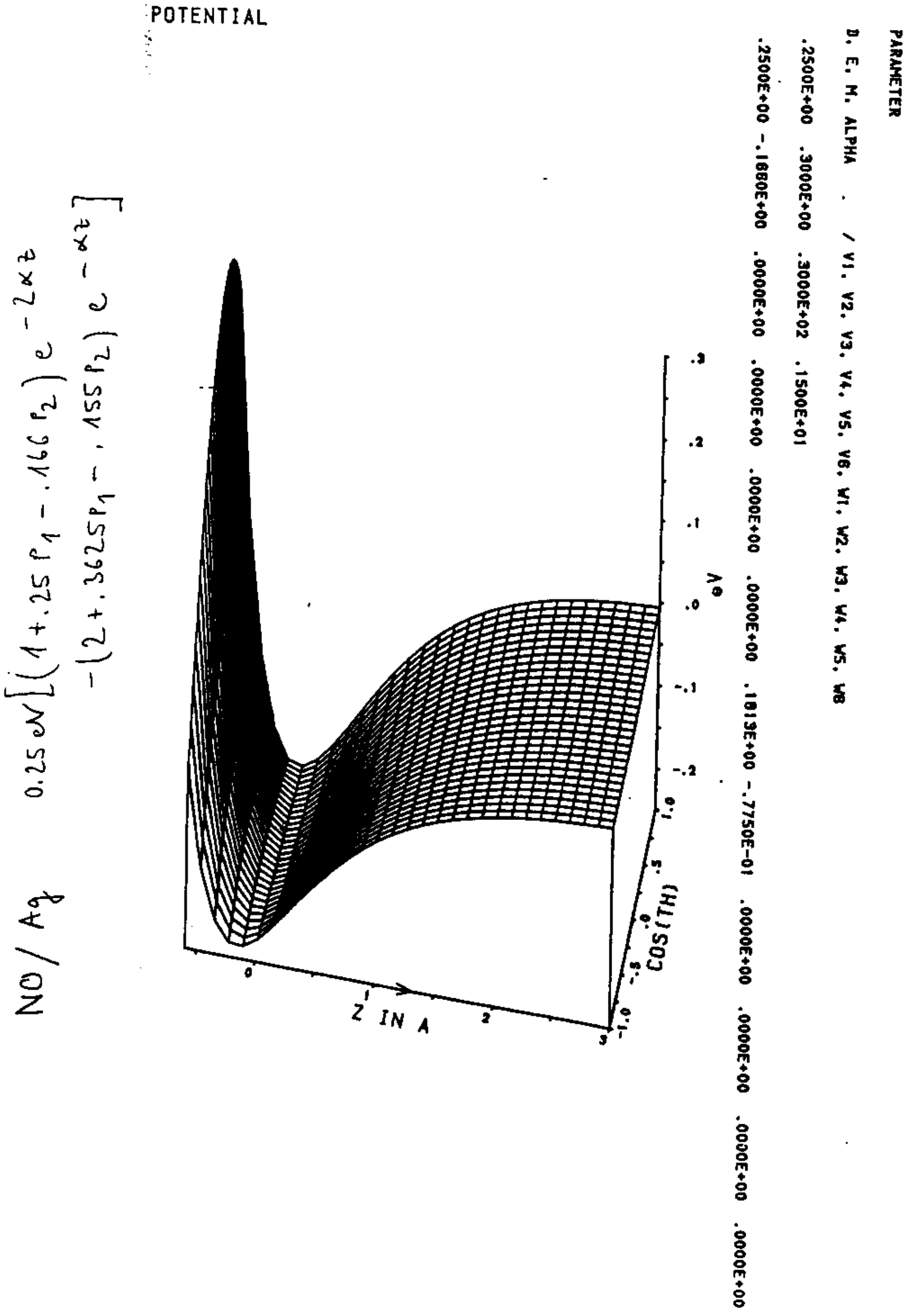


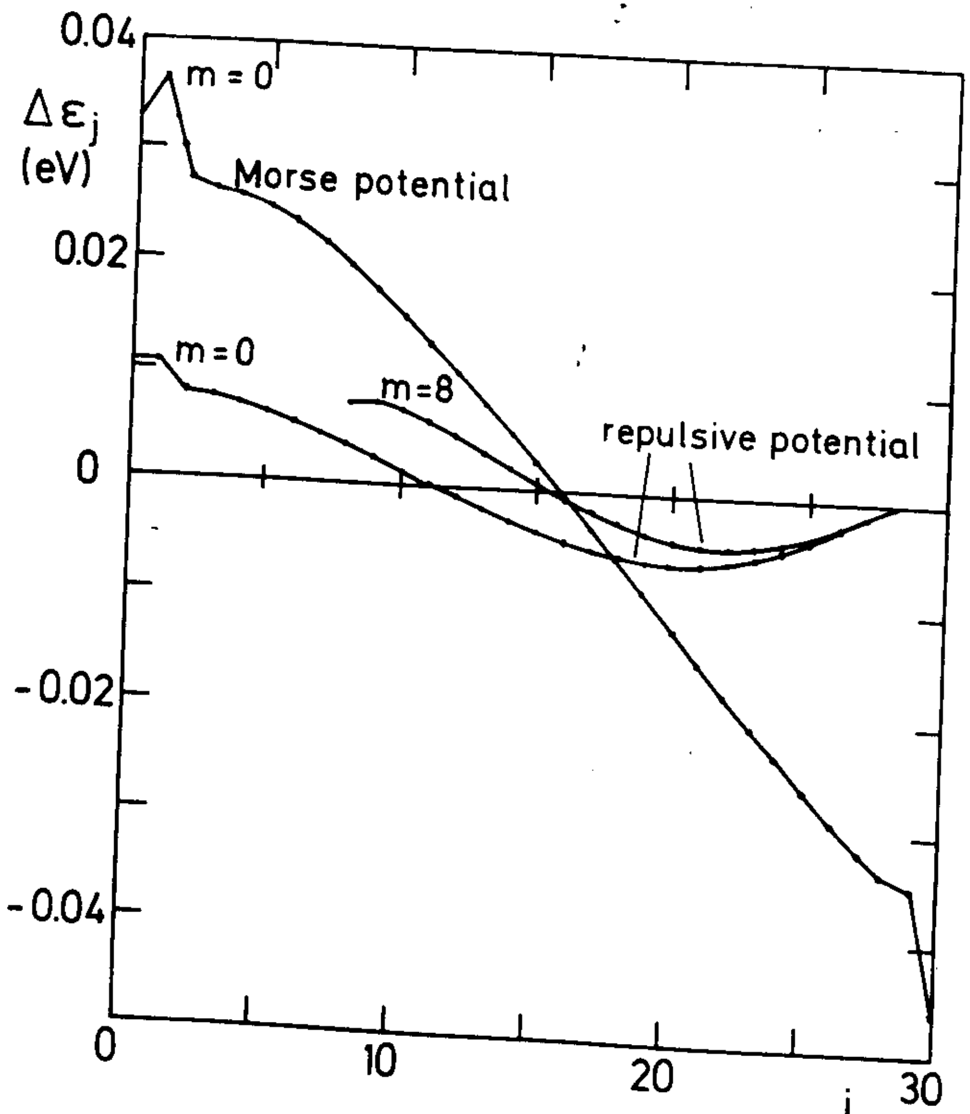
Fig. 5. Rotational temperatures of NO desorbing from Pt(111). The data are representative of data published for (×) neat thermal desorption[10a], (+) thermal desorption in the presence of coadsorbed CO[10b], (solid squares)[24] and (solid triangles)[25] trapping/desorption in molecular beam scattering, (open triangle) reaction limited desorption from NO–NH_3 complexes[14], (open circle)[26] and (open square)[27] NH_3 oxidation reactions. The solid line is for full accommodation. The dashed curve represents results for translational energy measurements in direct inelastic scattering[18b].

Schröter, David, Zacharias; Surf. Sci (to be publ.)









Br., Kasai, Müller (Surf. Sci 161 608 ('85))

Remarks concerning rotational cooling

from kinetic theory (detailed bal.)

$$P_j^{des} \propto S(E_j)\,(2j+1)\,e^{-E_j/kT_s}$$

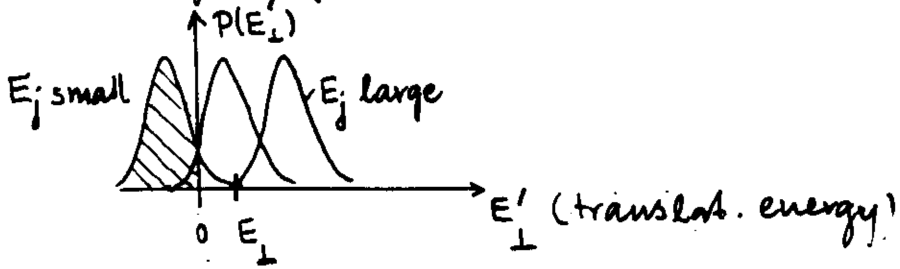
sticking coef. (from experim.)

$$S(E_j) \approx e^{-E_j/E_0}$$

effective temperature

$$T_{eff} = T_s \frac{E_0}{kT_s + E_0} \qquad E_0 \approx 400\ \mathrm{K}$$

Sticking coefficient (qualitatively)

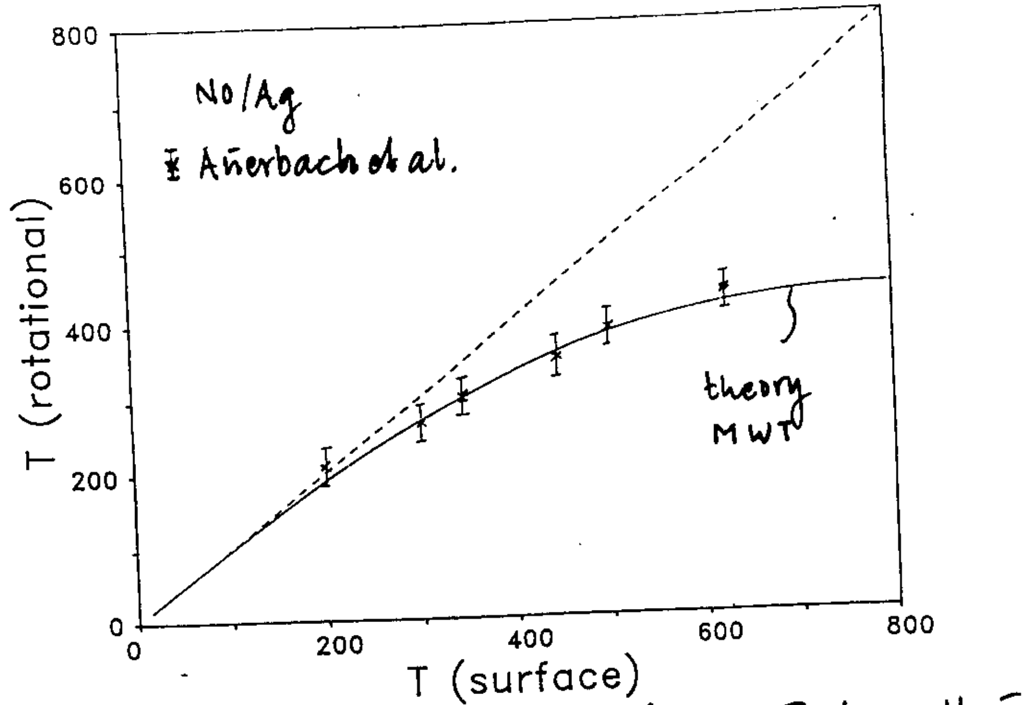


consider $\langle \Delta E_j \rangle = \langle E_j' \rangle - E_j \rightarrow$

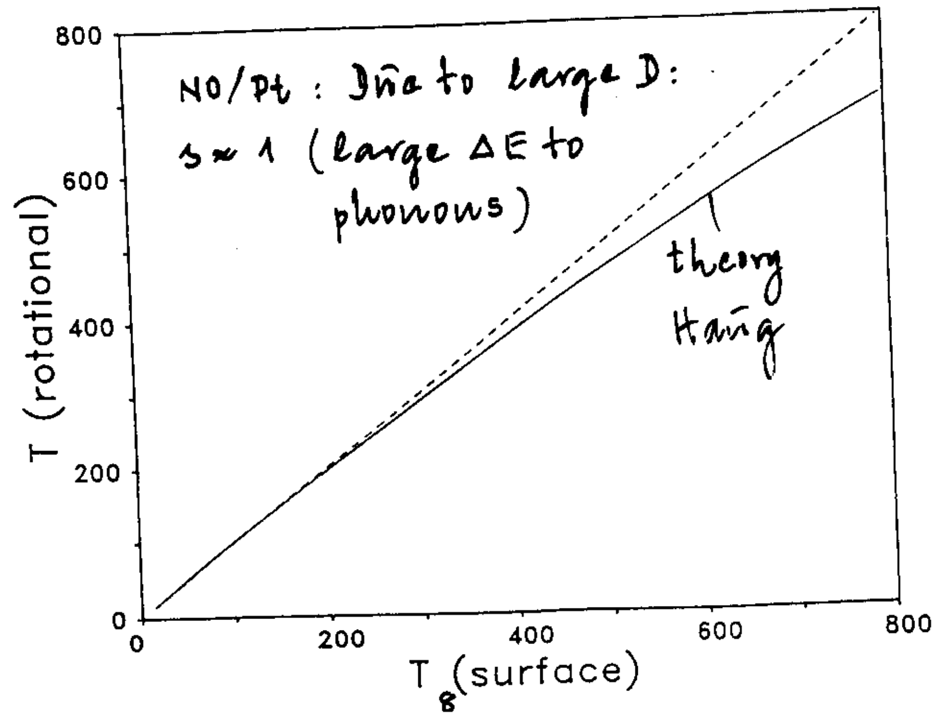
$E_0 \approx$ Energy E_j where

$$\langle \Delta E_j \rangle = 0$$

Question: Phonons?



Theorie: Muhlhausen, Williams, Tully; Hand



a) Detailed balance may be violated for two or more low lying modes of kinetic equation; in principle possible but difficult to obtain microscopically.

b) Very strong angular dependence of potential in contrast to

α) Direct scattering rotational energy distribution (Jacobs et al.)

β) steric effect of $s(\vartheta)$ (Kuipers, Tenner, Kleyn, Stolte)

$$\frac{2(s_- - s_+)}{s_+ + s_-} \approx 0.035 \pm 0.02$$

γ) $A(2) \approx \langle 3m^2 - j(j+1) \rangle$ (Jacobs et al.)

all can be accounted for by

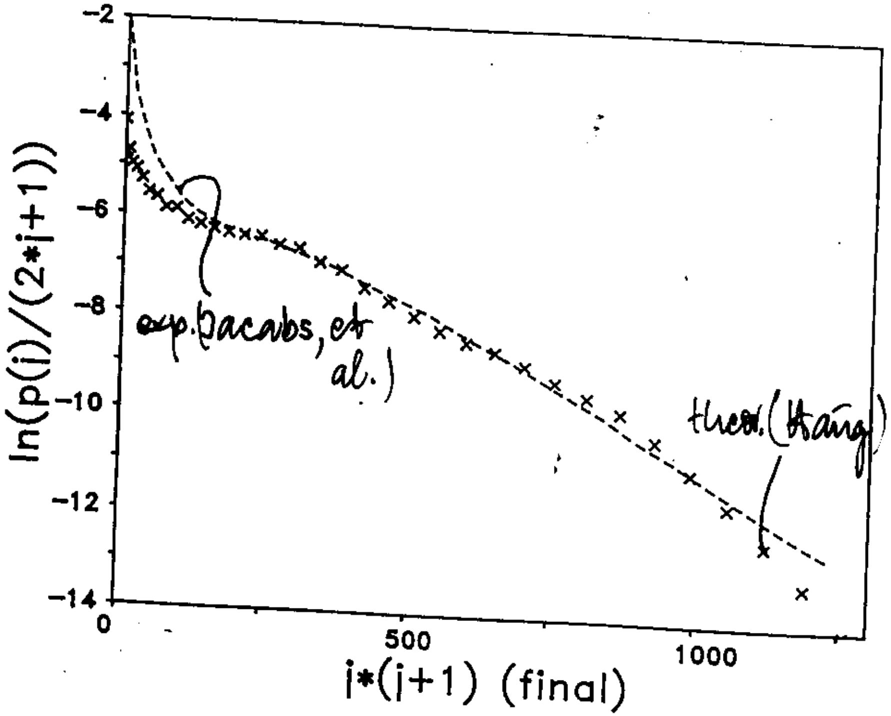
$$Y(\vartheta) = D\{R(\vartheta)e^{-2\alpha z} - A(\vartheta)e^{-\alpha z}\}$$

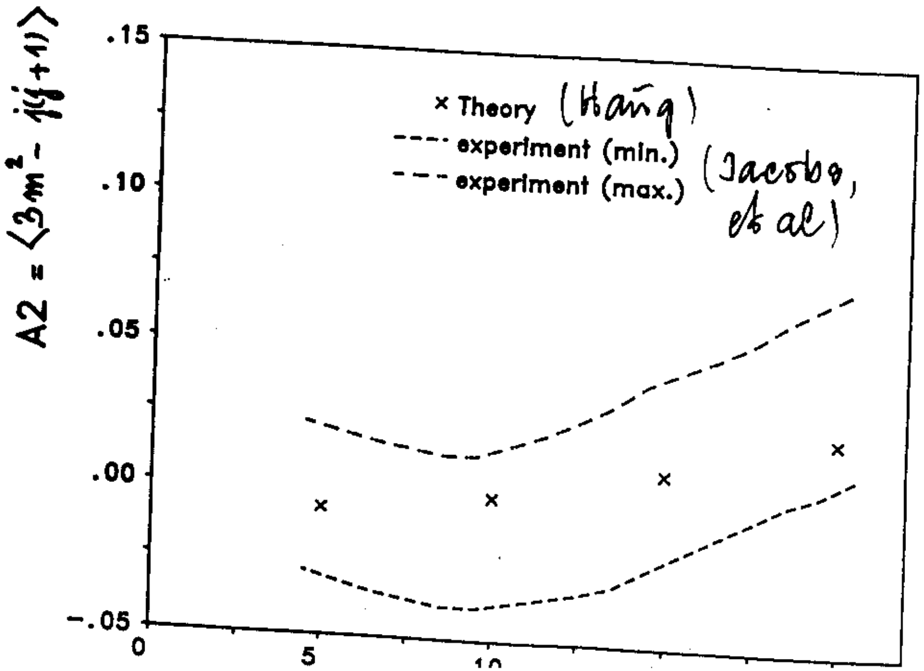
$$R(\vartheta) = 1 + 0.075\,P_1(\cos\vartheta) + 0.075\,P_2(\vartheta)$$

$$A(\vartheta) = 2\,(1 + 0.06\,P_1(\vartheta) + 0.075\,P_2(\vartheta))$$

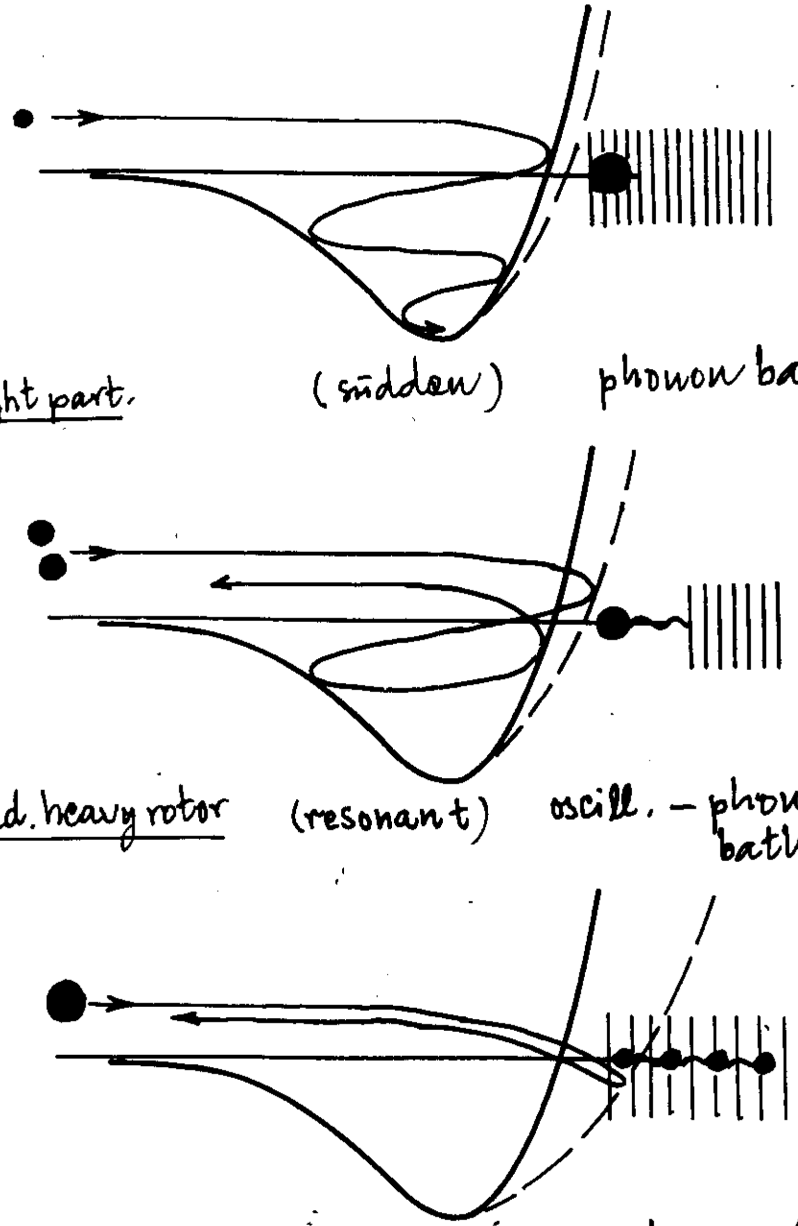
c) Selective Scattering Resonances

$$s(E_j) \approx \sum P_r \frac{\Gamma_{inel}}{a\Gamma_{inel} + \Gamma_{el}}$$



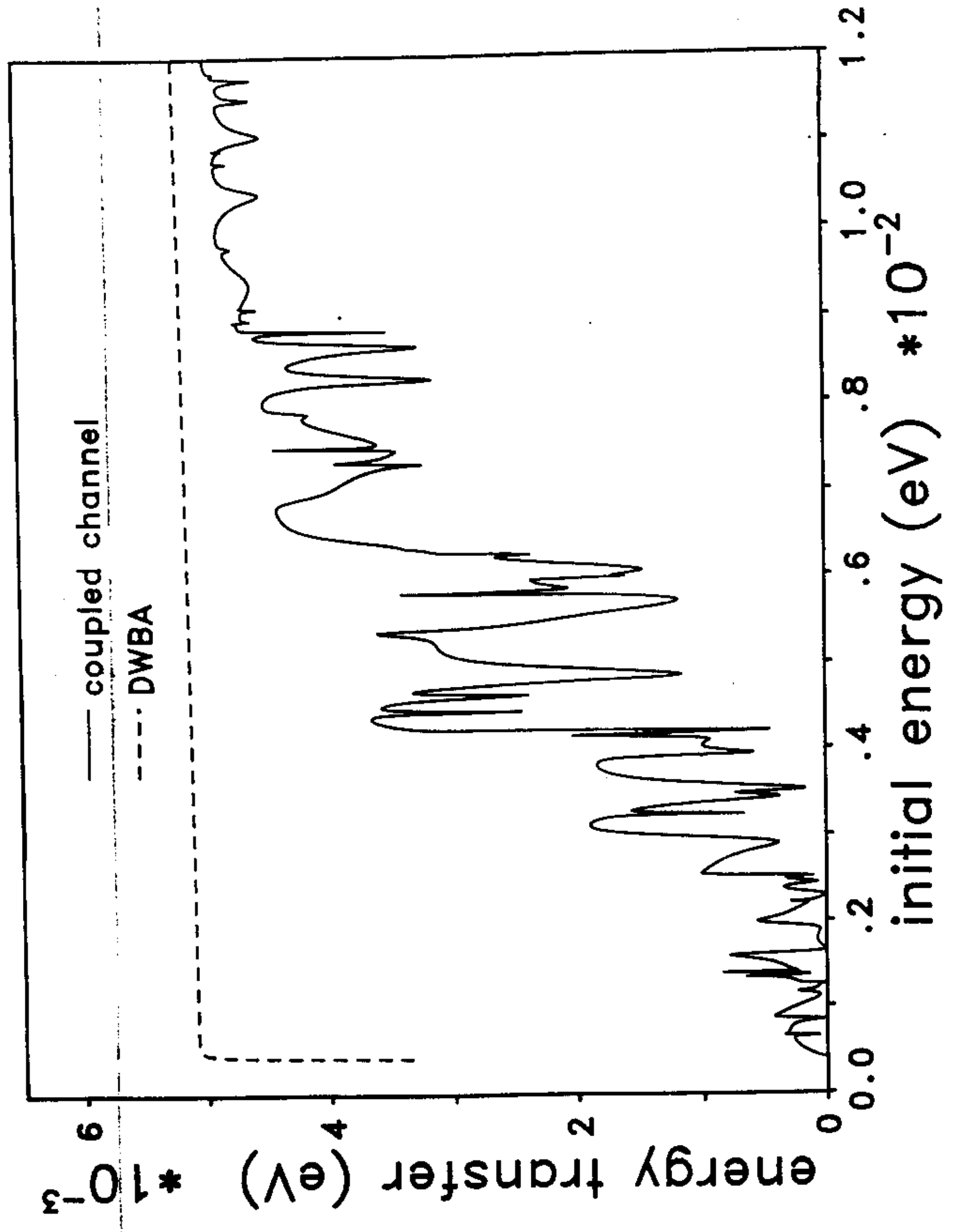


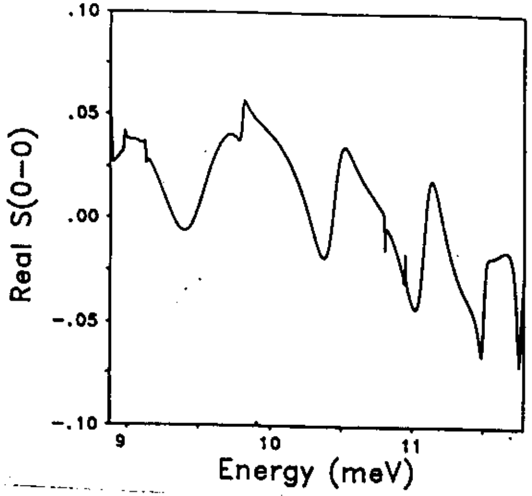
Time scales for sticking (schematic)



(Levi, Sühl, Kohn, ..., Günther br)

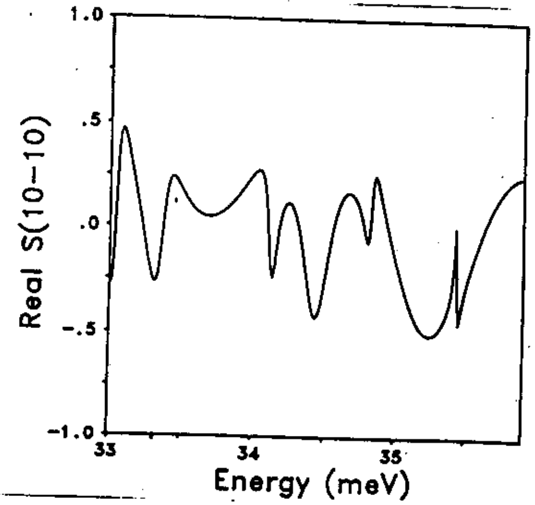
selective rotational resonances (Brünner)



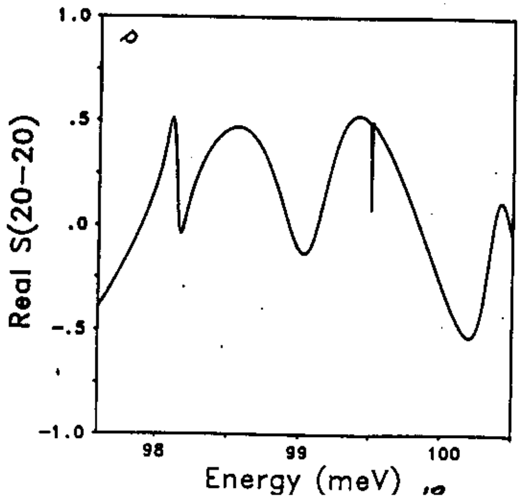


$j_{im} = 0$

Increase of rot. reson. width with j_{im}



$j_{im} = 10$



$j_{im} = 20$

T. Brunner

<u>Model for</u> vib.-trans. coupling

<u>Neglect</u>:

- Rotations
- Corrugation
- Phonons (NO?)

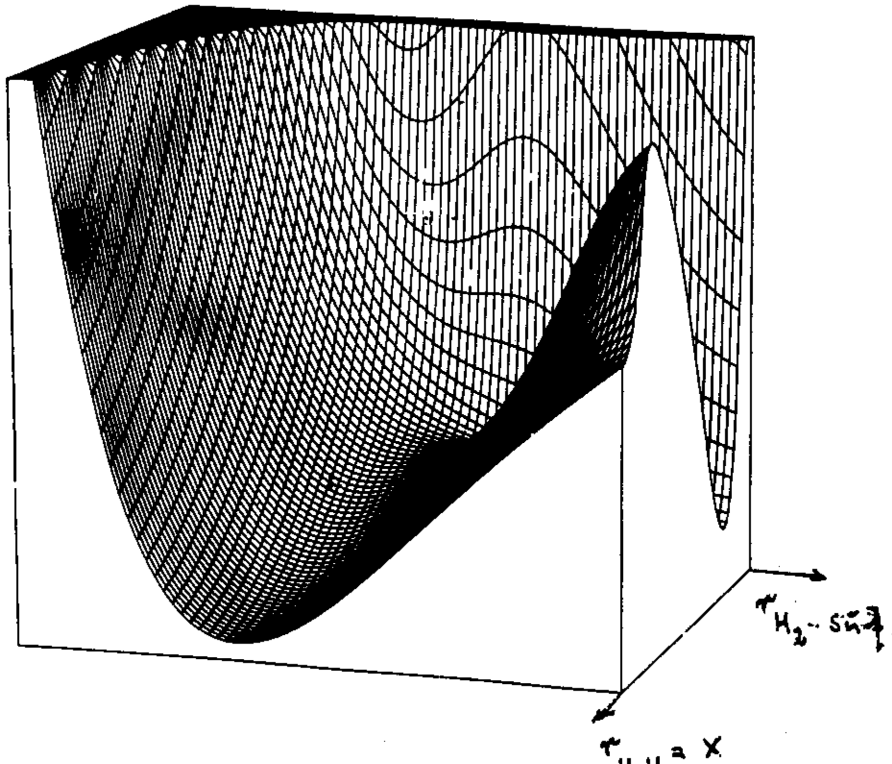
→

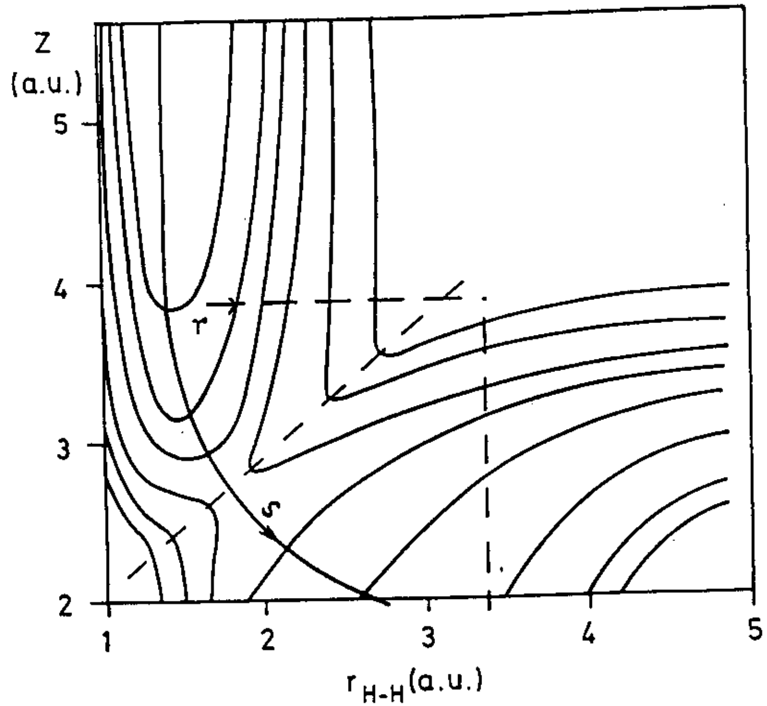
<u>2 D-PES</u>, Parameters:

- Barrier $V(s)$
- Curvature $c(s)$ (Change in bond length)
- Frequency $\omega(s)$

Potential Surface for

H_2/Cu





Schrödinger equation (harmonic appr. for vibration)

$$\{-\frac{\hbar^2}{2\mu} D_s \eta^{-1} D_s + \eta[V(s) + \hbar\omega(s)n - E]\} \psi(r,s) = 0$$

with curvelinear differential operator

$$D_s = \partial_s - \frac{\omega'(s)}{2\omega(s)} r\, \partial_r$$

coupling term

$$\eta(r,s) = 1 - C(s)\, r/\,\kappa(s) \qquad C(s) = \text{curvature}$$

vibrational wave number

$$\kappa(s) = (\mu\omega(s)/\hbar)^{1/2}$$

Scattering Amplitudes

Desorption (state selective)

m $\quad D_{nm}$ $\}n$

$n\{$ R'_{nm}

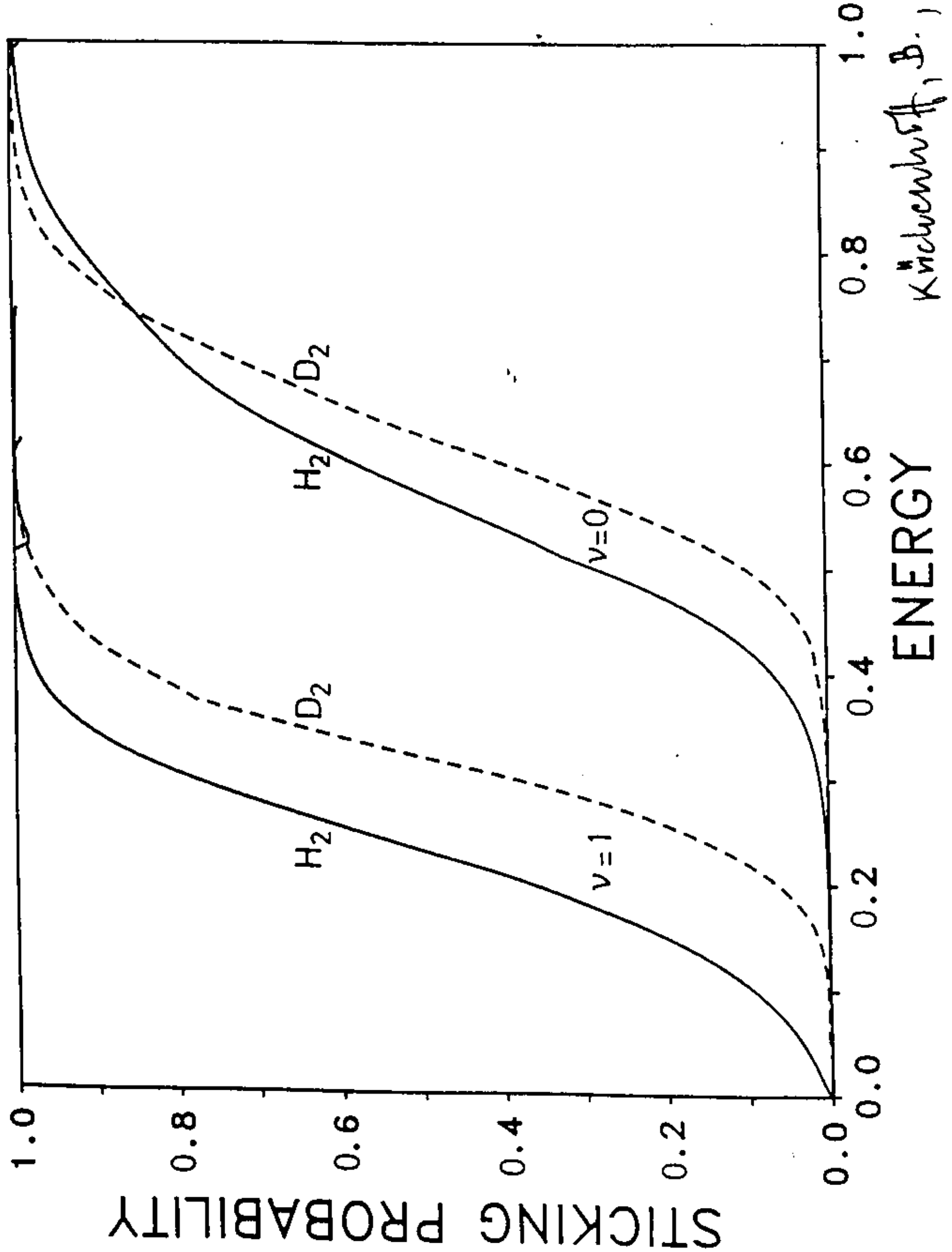
Sticking (state selective)

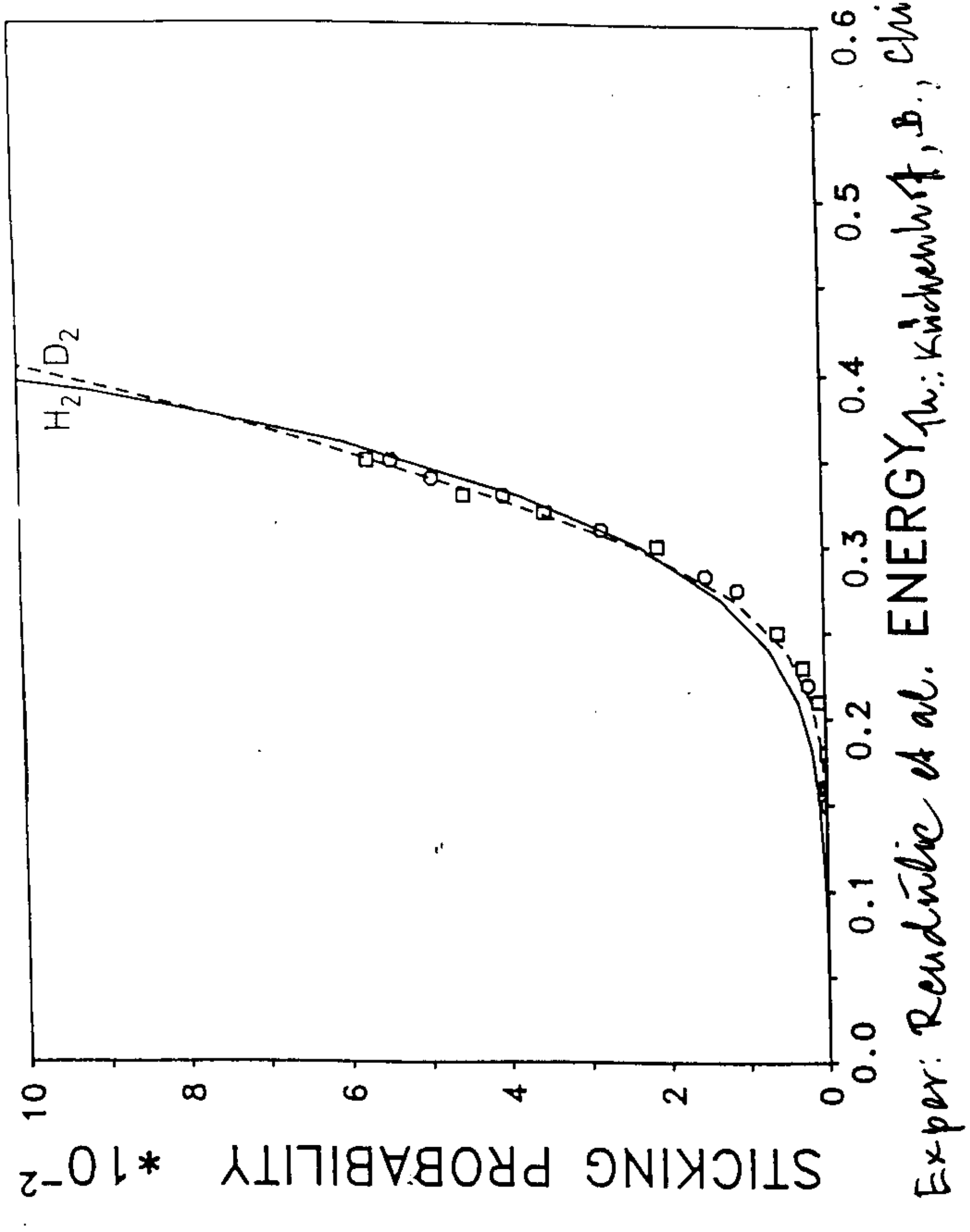
$n\{$ S_{mn} $\quad m$

$\}n$ R_{nm}

Detailed Balance (time rev. inv.)

$$D_{nm}(\varepsilon_{tot}) = S_{mn}(\varepsilon_{tot})$$

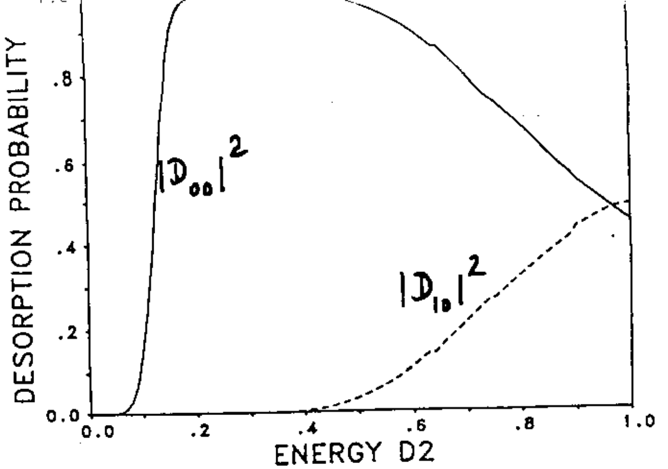


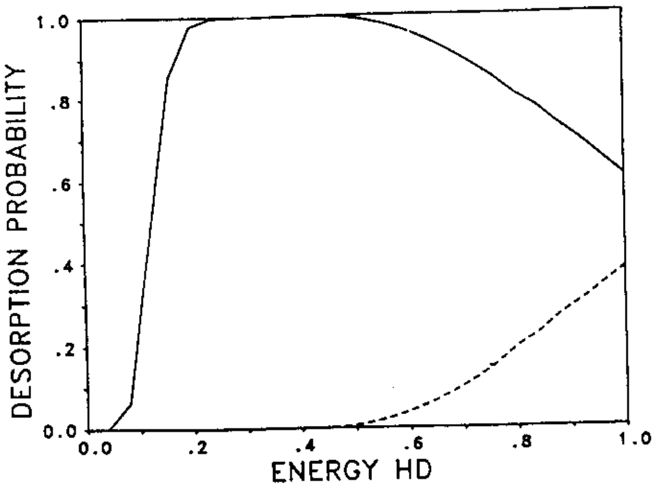


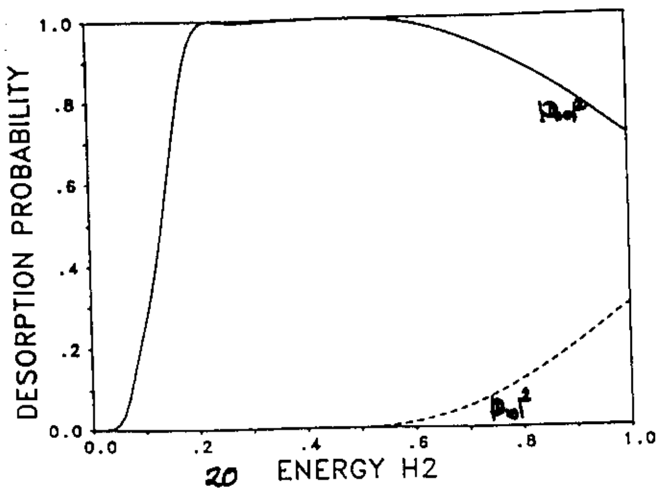
Hydrogen/Pd

Exper.:
Schröter,
David,
Zacharias

Theor.:
Kirchenhoff, B.,
Kasai





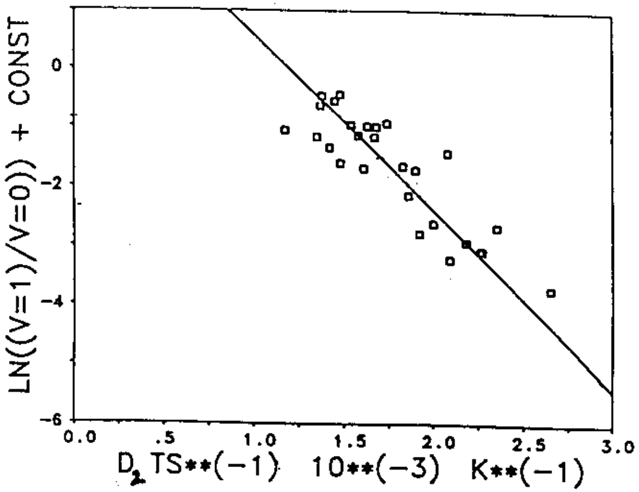


E_a

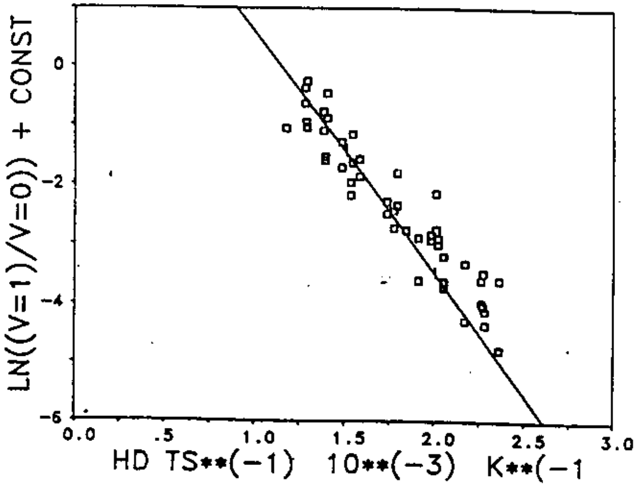
Hydrogen/Pd

Exper.: Schröter, David, Zacharias

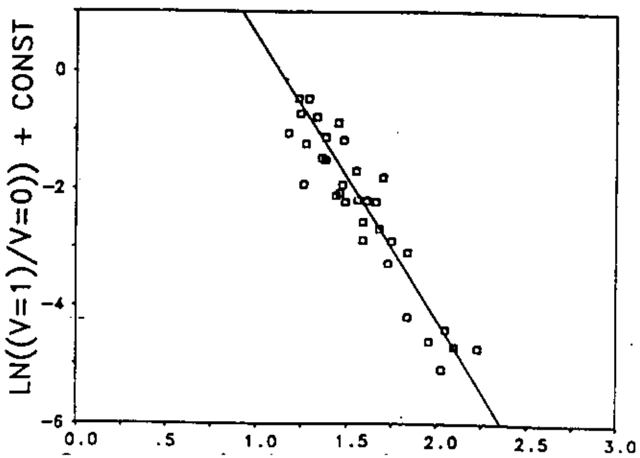
Theor.: Kirchenhoff, B.



234 meV (371)



282 meV (450)



428 meV (517)