united nations educational, scientific and cultural organization

international atomic energy agency

the
abdus salam
international centre for theoretical physics

SMR/1238-24

ADRIATICO RESEARCH CONFERENCE on

LASERS IN SURFACE SCIENCE

11-15 September 2000

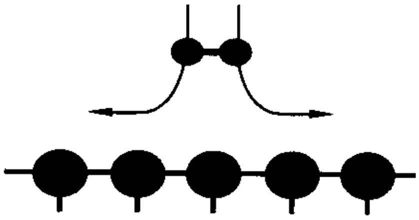
Miramare - Trieste, Italy

Nitrogen formation at metal surfaces

Andrew Hodgson
University of Liverpool
Liverpool, United Kingdom

Nitrogen formation at metal surfaces

A. Hodgson

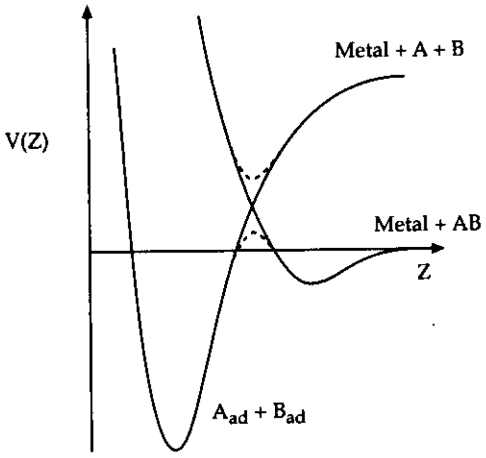


Surface Science Research Centre
The University of Liverpool

Mike Murphy, Cu(111)
John Skelly, Ru(001)
Paul Samson Pd(110)

Diatomic Dissociation Dynamics

"LIGHT"



- * Weak coupling to phonons.
- * No chemisorption well.
- * Dissociation is usually direct.

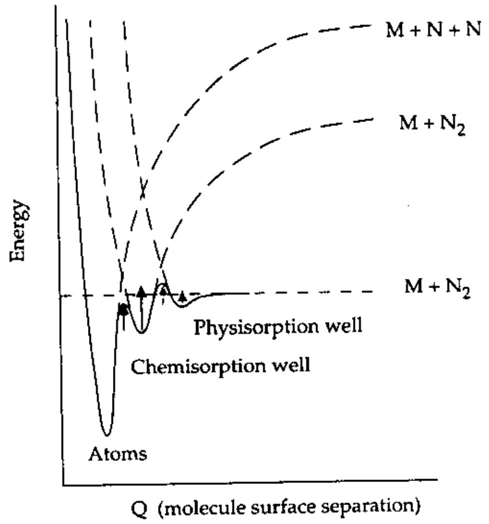
Quantum state directly influences sticking.

Tells us about:

the shape of the PES,
where the barrier lies,
the curvature (Z,r) near the barrier,
the range of the attractive well.

"HEAVY"

- * Efficient coupling to phonons.
- * Deep chemisorption/ physisorption well(s).
- * Dissociation is often indirect, trapping-dissociation.
- * Complex minimum energy paths.
- * Kinetic models important

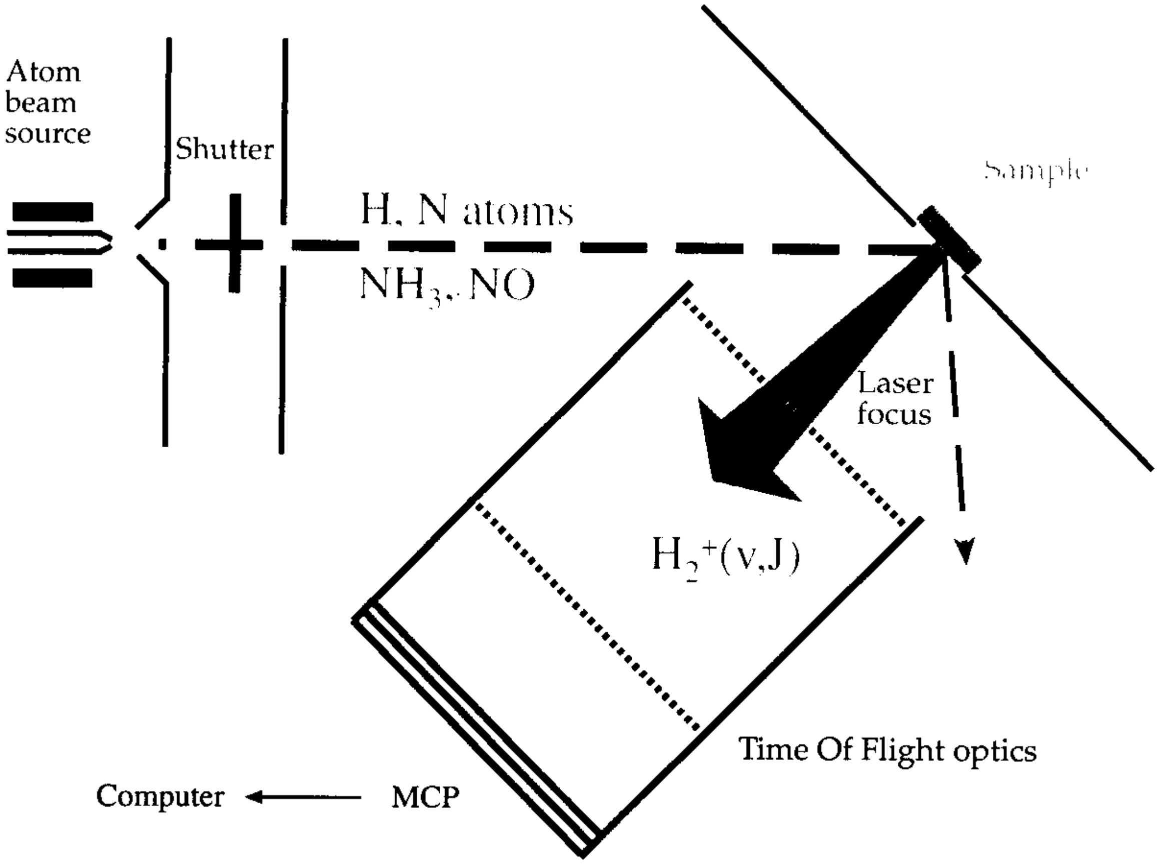


Does molecular quantum state directly influence sticking?

Do molecular wells scrample internal energy?

Can we learn about the shape of the PES from state resolved experiments?

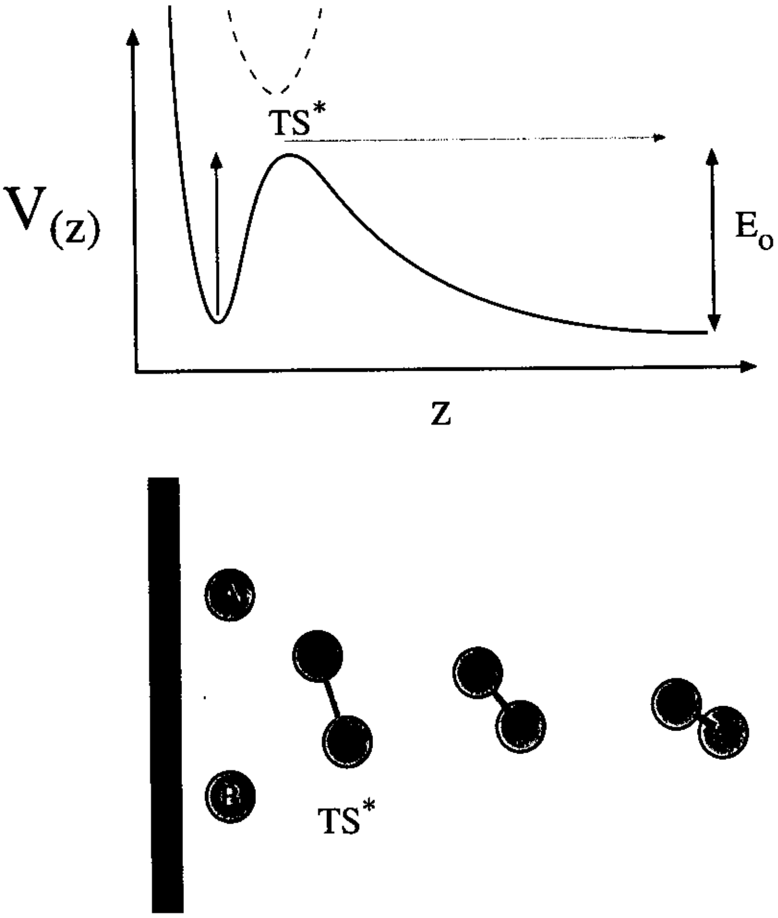
- Measure $P(v, J, E, T_s)$ for recombinatively desorbed molecules using REMPI - TOF.



- Dose N atoms on front surface and control T_s.
- TOF distributions using a weak extract field allow accurate background subtraction.
- Can be used for a wide variety of reactions;

$H + H \rightarrow H_2$	Cu, Pd, Ag, Ni reaction of surface and sub-surfac species.
$N + N \xrightarrow{Cu(111)} N_2$	Murphy, Skelly & Hodgson, Chem. Phys. Lett., **279** (1997) 112 J. Chem. Phys., **109** (1998) 3619
$2NH_3 \xrightarrow{Ru(0001)} N_2 + 3H_2$	Murphy, Skelly, Hodgson & Hammer J. Chem. Phys. 110 (1999) 6954
$2NO + 2H_2 \xrightarrow{Pt(111)} N_2 + 2H_2O$	Sampson, Murphy & Hodgson, in prep.

Interpretation of product state distributions?

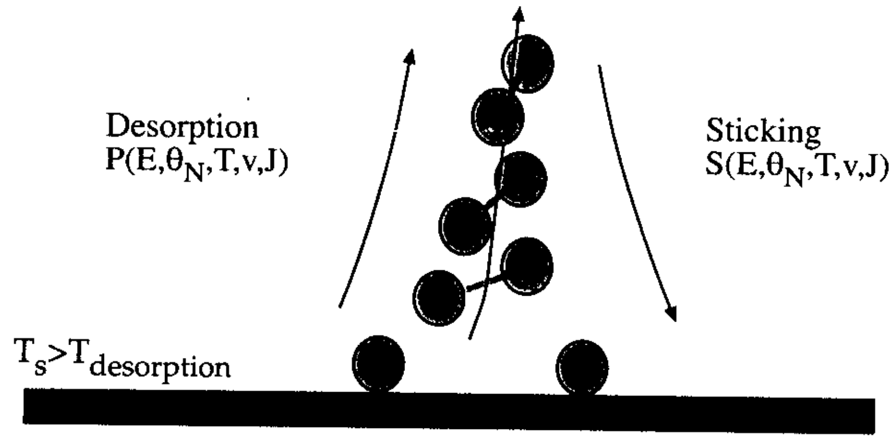


Thinking of the product state distributions as resulting from scattering from a well defined transition state is dangerous!

Desorption is excited THERMALLY by excitation from the surface.

Must treat the statistical nature of the process.

Recombinative Desorption:



- Detailed Balance

$$P(E,v,J;\theta_N,T) \propto \underbrace{E\exp(-E/kT)\exp(-\varepsilon_{v,J}/kT)}\;S(E,v,J;\theta_N,T)$$

Energy & State distribution for recombinative desorption

Thermal energy available

Sticking probability as a function of energy and internal state

- Recombinative desorption is driven by thermal excitation of the surface, heat bath supplying excitation at ~10^{13} s^{-1}.

If S is independent of (v,J) the state distribution will be thermal.

P(E) is a convolution of the thermal energy and S(E).

- The surface coverage is not the same as at equilibrium.

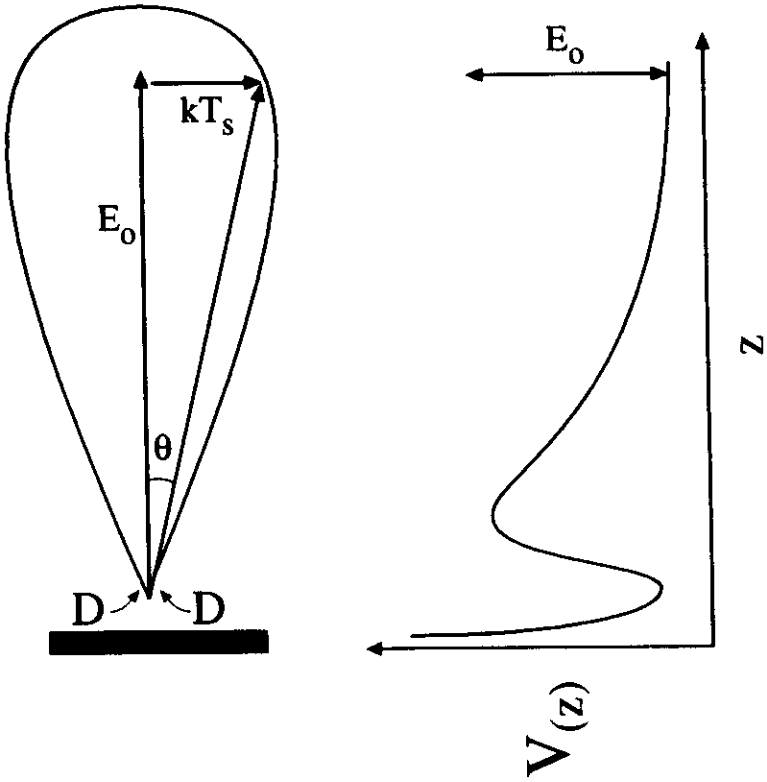
The total energy available is indeterminate (unlike most gas phase systems)

Angular Distributions

Detailed Balance:-

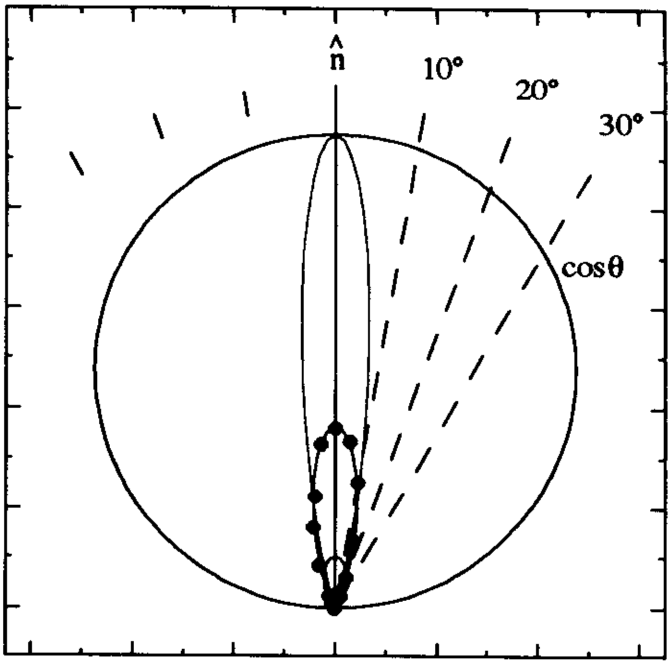
$$P(\theta, T) = \int_0^\infty \frac{1}{N_E} E \exp^{-E/kT} \cos\theta \, S_0(E, \theta; T) \, dE$$

Van Willigan, 1968
Assume energy barrier E_o perpendicular to surface;
Motion || to surface has no effect;

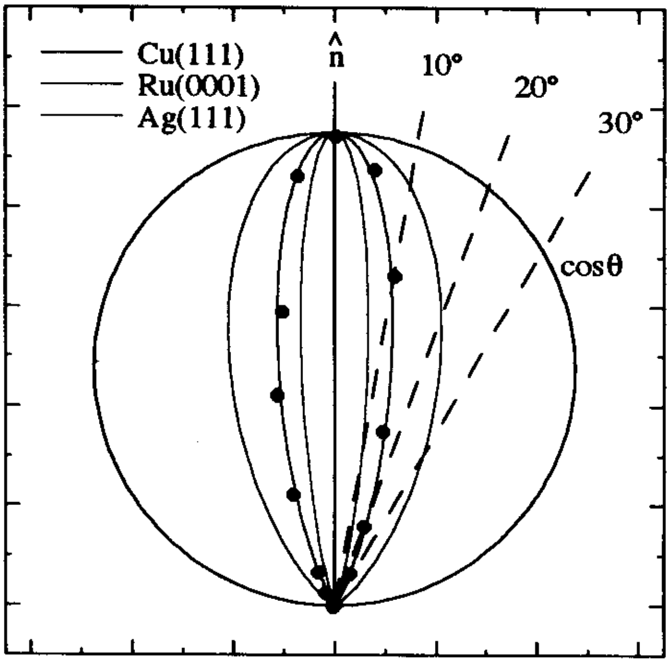


$$P(\theta) = \frac{(E_o + kT\cos^2\theta)}{(E_o + kT)\cos\theta} \exp^{-(E_o \tan^2\theta)/kT}$$

Angular N_2 Distributions



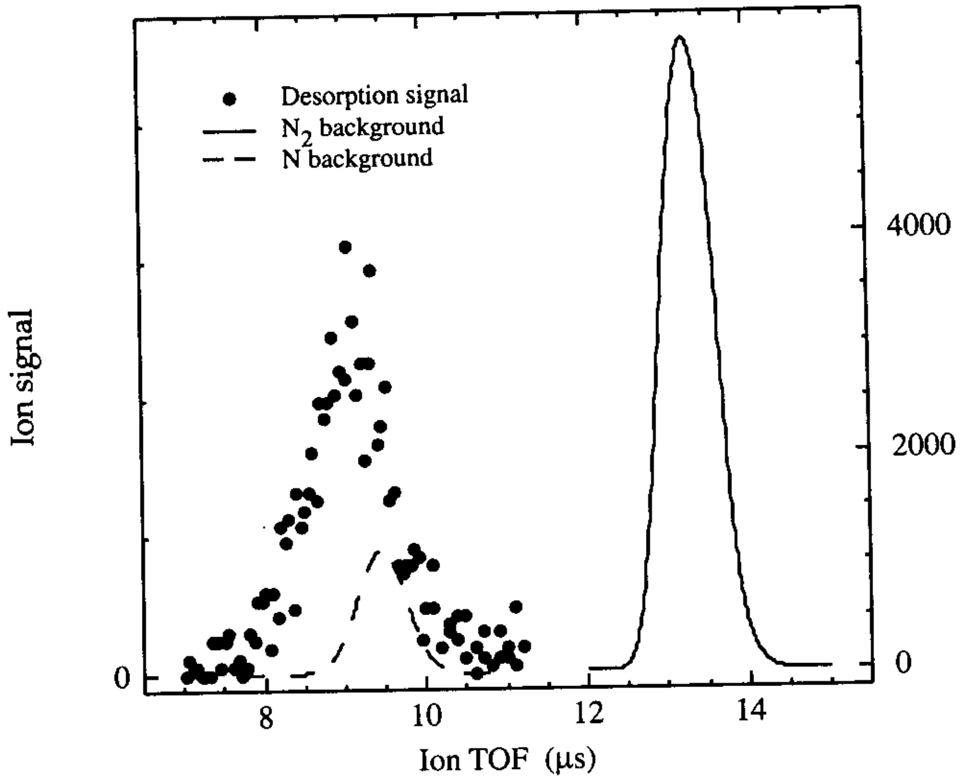
$P(\theta) = \cos^{28}\theta$
$\cos^{8}\theta$
$\cos^{75}\theta$
$\cos^{1}\theta$



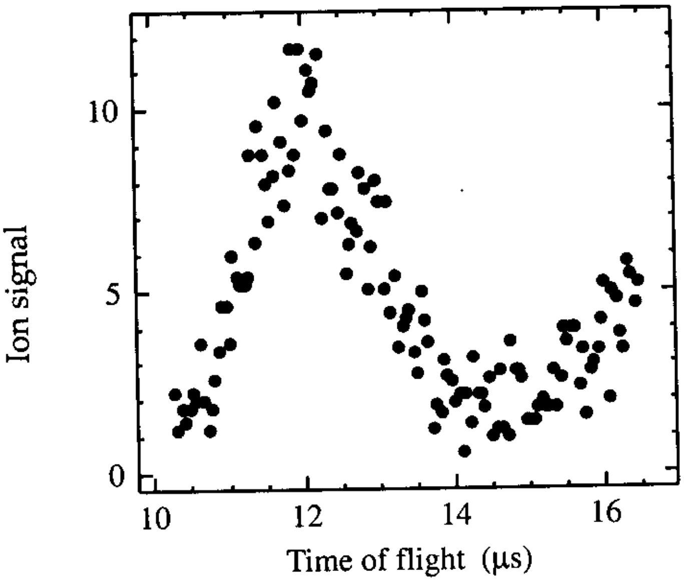
Cu(111) - J. Chem. Phys. 109 (1998) 3619
Ag(111) - Surf. Sci. 387 (1997) 102
Ru(0001) - Matsushima, Surf. Sci. 192 (1988) L287
Pd(110) - Tanaka

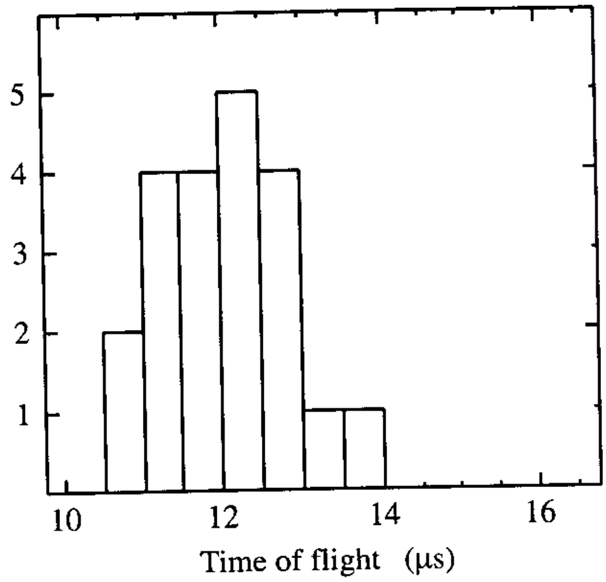
TOF distributions for N_2 recombination at Cu(111).

- $N_2(v=0)$ + thermal background.



- N_2 (v=1) continuous desorption.
- N_2 (v=0) flash desorption, ~4 ML.

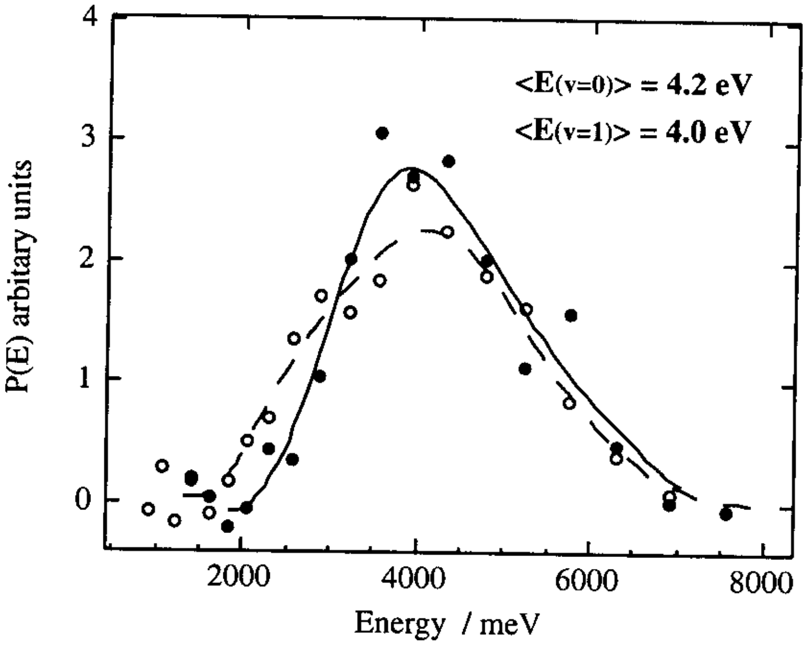


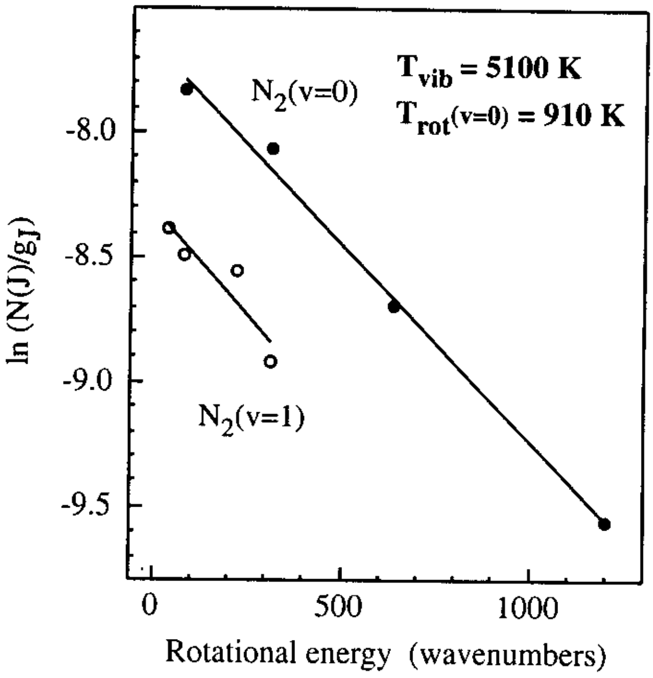


- TOF distributions calibrated using a thermal knudsen source.

Energy Disposal: N_2 from Cu(111)

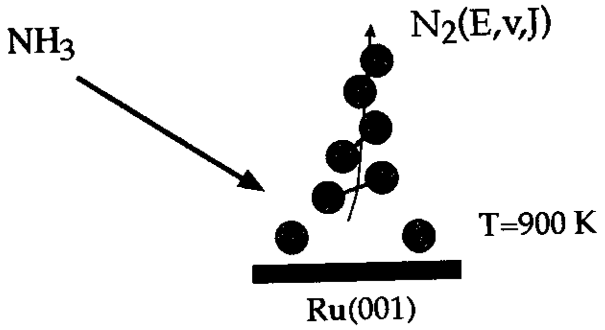
T_S=700 K

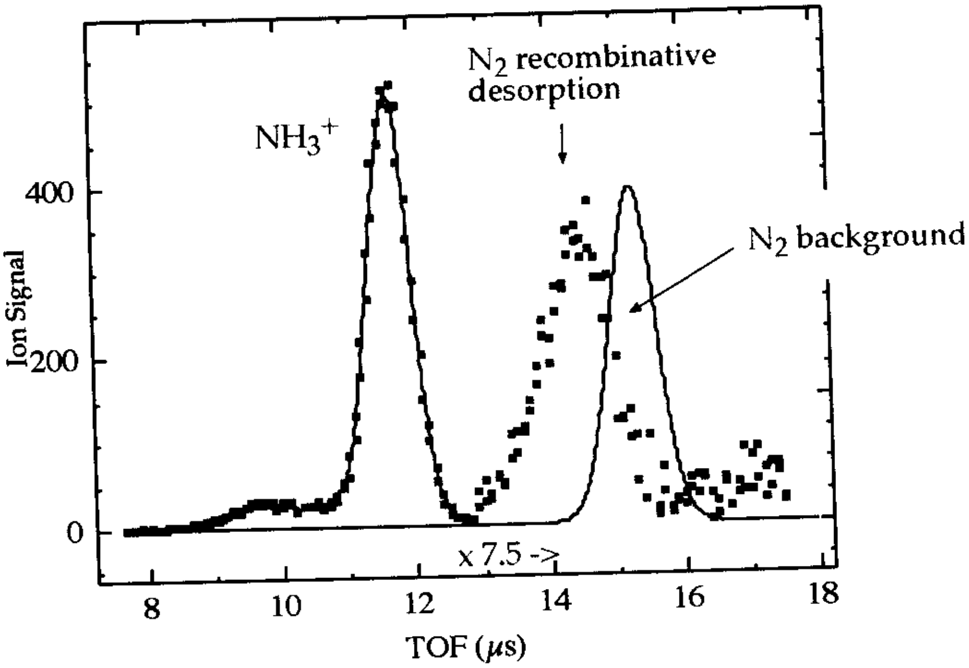




N_2 Recombinative Desorption from Ru(0001)

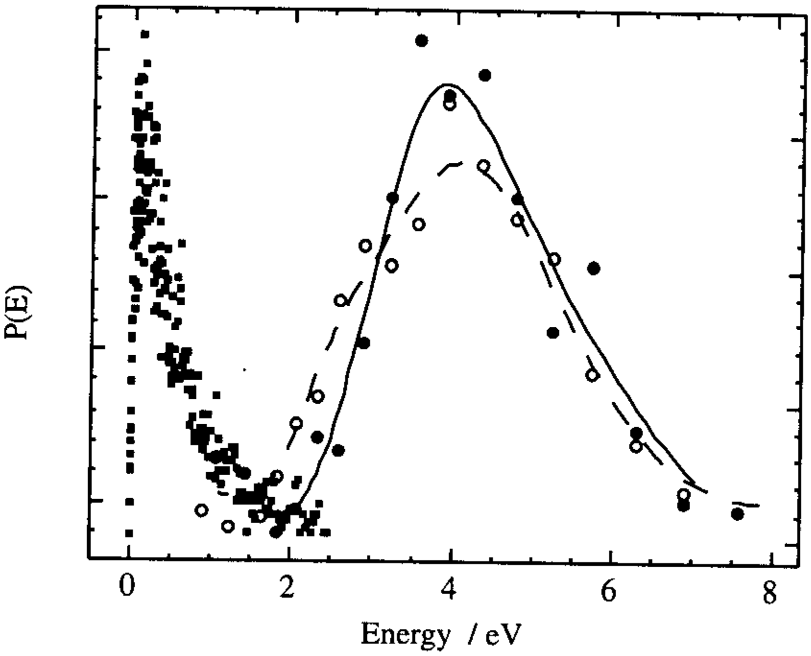
Experiment

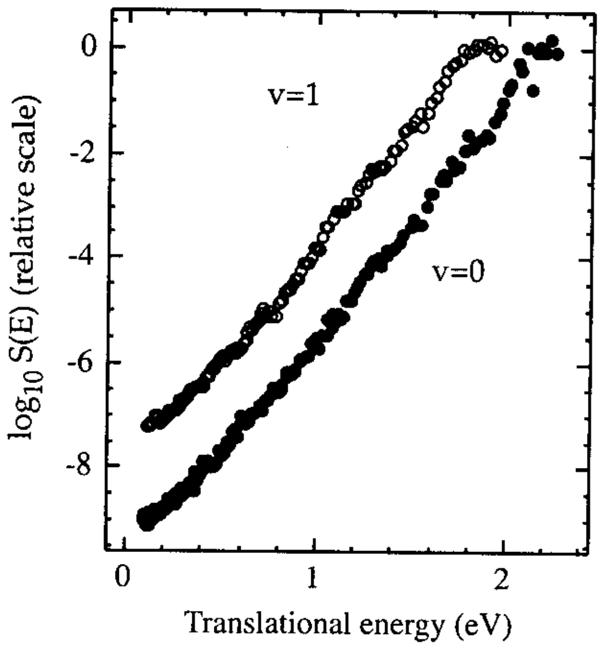




- Mean translational energy release 0.61 eV for $N_2(v=0)$ and 0.60 eV for $(v=1)$.
- Vibrational distribution is inverted with a population ratio $N_2(v=1)/(v=0) = 1.4 \pm .2$
- Rotation is cooled, $T_{rot}=630$ K.

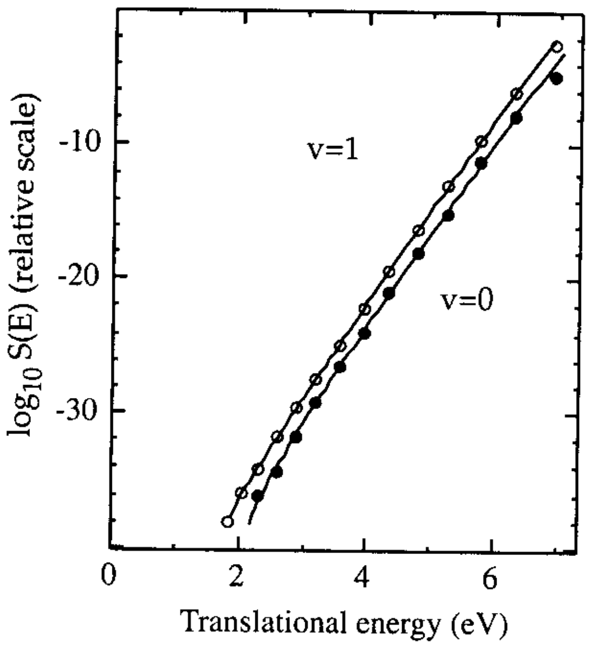
Predicted sticking functions for N_2-Cu(111)/Ru(0001




Ru(0001)

Sticking increases from < $10^{-8.5}$ at low energy with a pronounced low energy tail.

Vibrational efficacy 1.3

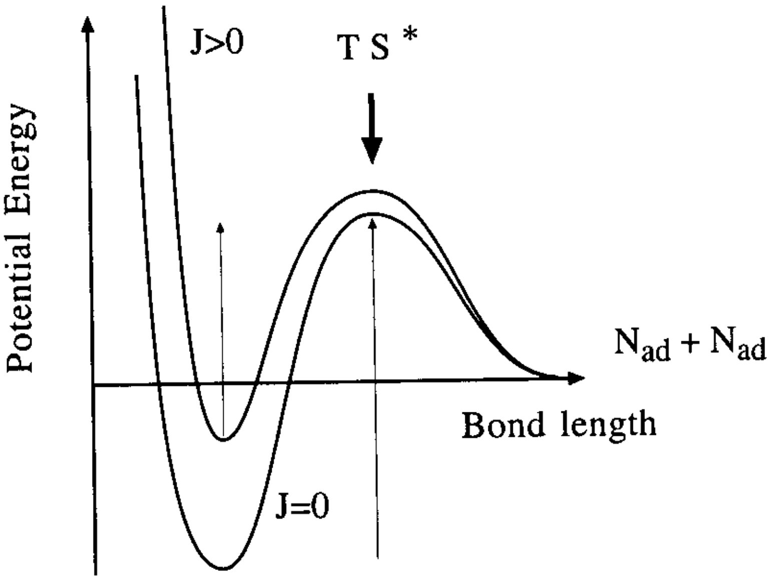

Cu(111)

Sticking increases exponentially near 4 eV with no low energy tail.

Vibrational efficacy ~0.7

Influence of rotation on adsorption/desorption

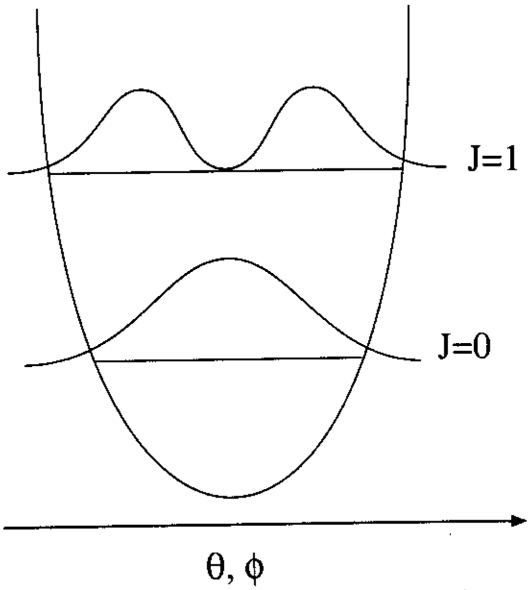
- **Extended transition state:** $E_{rot} \propto h^2/(8\mu\pi^2)J(J+1)$ $(1/r^2)$



Desorbed N_2 molecules are rotationally excited.

Rotation aids sticking.

- **Constrained transition state: - hindered rotor.**



Classically:- steering into the preferred orientation is hindered by rotation.

Desorbed N_2 molecules are rotationally cold.

Rotation aids sticking.

Quantum:- constrained TS mixes J states.

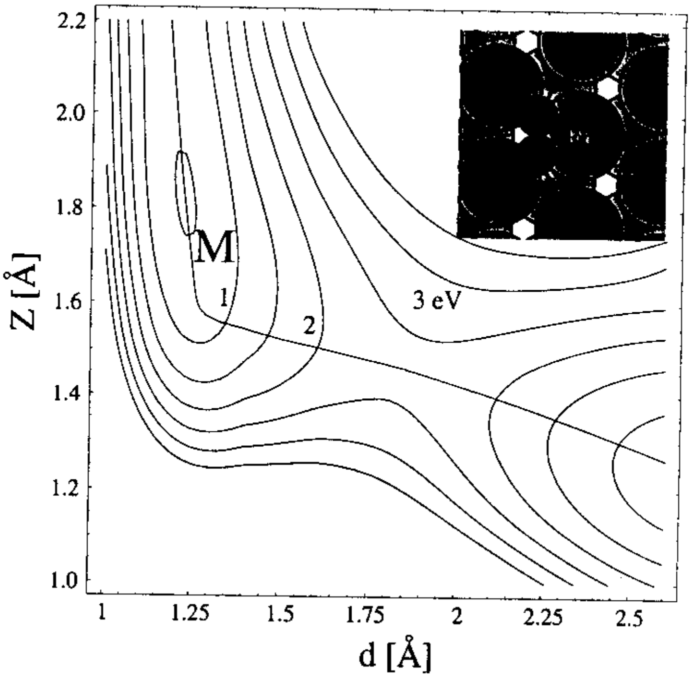
Desorbed N_2 molecules are rotationally excited.

Rotation aids sticking.

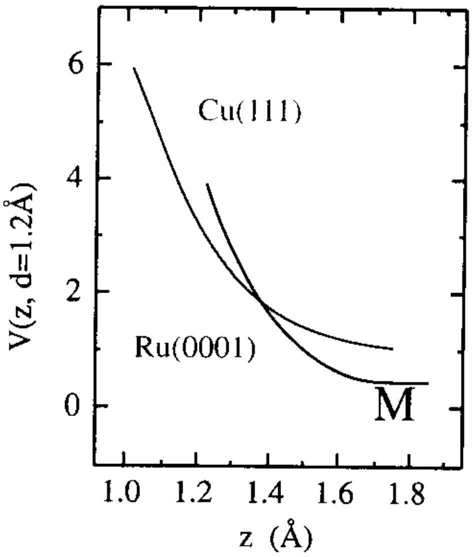
Potentials for N_2 dissociation on Cu(111) and Ru(0001)

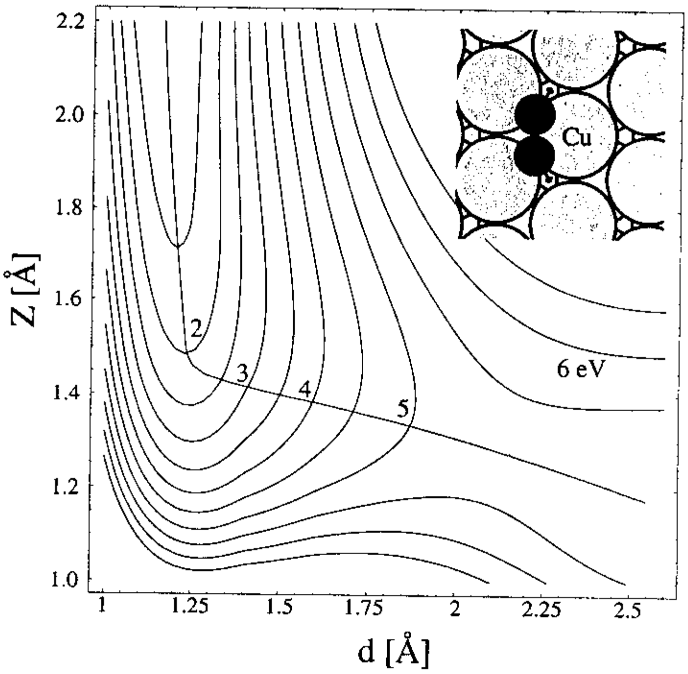
Bjørk Hammer,
DFT potentials for N_2 dissociating in a planar geometry with N moving from the bridge to the hcp hollow site.

Ru(0001) shows a well due to a metastable chemisorption state, marked 'M' Mortensen *et al.*
(J. Cat. 169 (1997) 85)



N_2-surface repulsion.





Desorption Energetics

- N_2/Cu(111) Energetics

  Translational energy of $N_2(v=0)$ is comparable to the barrier height. Total energy of $N_2(v=1)$ is slightly larger than v=0, reflecting the lower efficiency of vibration compared to translation for sticking.

- N_2/Ru(001) Energetics

  Translational energy of $N_2(v=0)$ is 0.61 eV, cf. minimum barrier of ~2 eV. Total energy of $N_2(v=1)$ is ~0.9 eV, despite the population inversion and the greater efficiency of vibration compared to translation in sticking.

- For E<1.8 eV the shape of S(E) is almost identical for $N_2(v=0)$ and (v=1).

  $$P(E,T) \quad \propto \quad E\exp(-E/kT) \quad . \quad S(E,T)$$

  hence translational energy release is similar for both states.

- Population inversion when:

$$\int E\, e^{-E/kT}\; S(E, v=1)\, dE \;>\; \exp^{-(\Delta\varepsilon_{vib}/kT)} \int E\, e^{-E/kT}\; S(E, v=0)\, dE$$

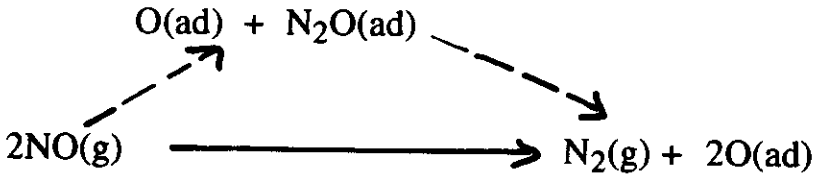
A population inversion will occur when the threshold for sticking is shifted by more than the vibrational quanta, - this is the case for Ru(0001) but not for Cu(111).

Dynamics of Simple Reactions

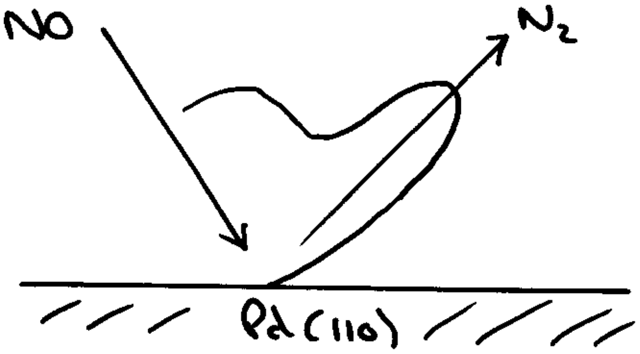
Scatter NO/N_2O from a surface and investigate the formation of N_2 products by REMPI

P(v, J) state distributions,
angular distributions.

Systems - <u>Pd(110)</u>
Cu(110)



Tanaka et al.
S.S.

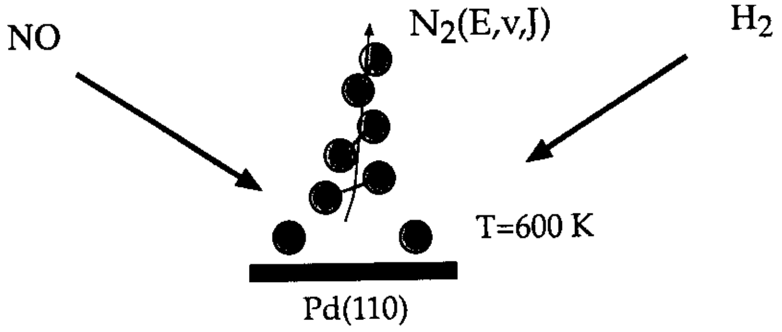


Clean the O(ad) off with H_2 or CO

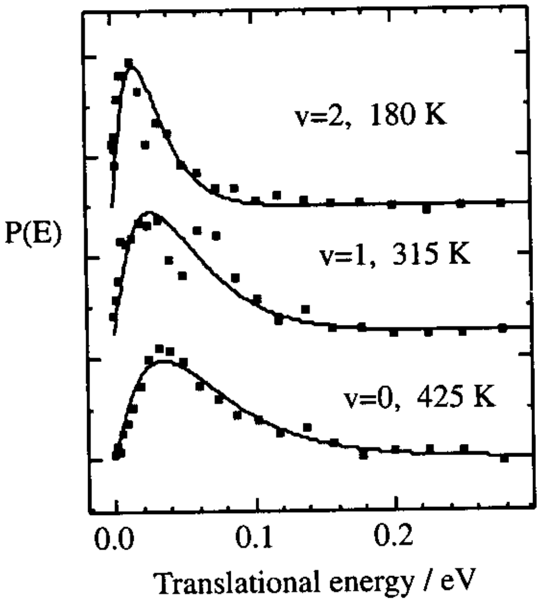
Effect of CO or O coadsorption and coverage on N_2 formation mechanism?

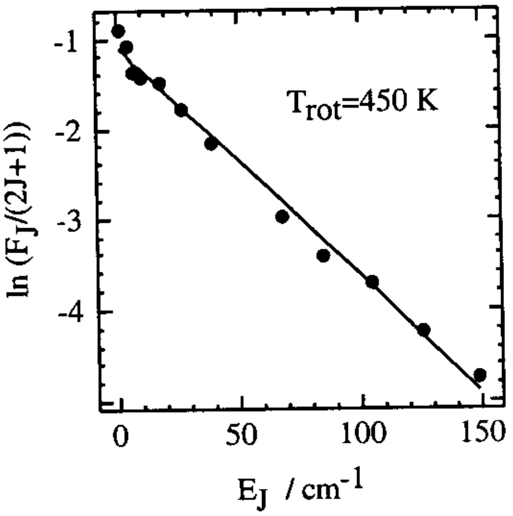
NO + H_2 Reaction at Pd(110)

Experiment



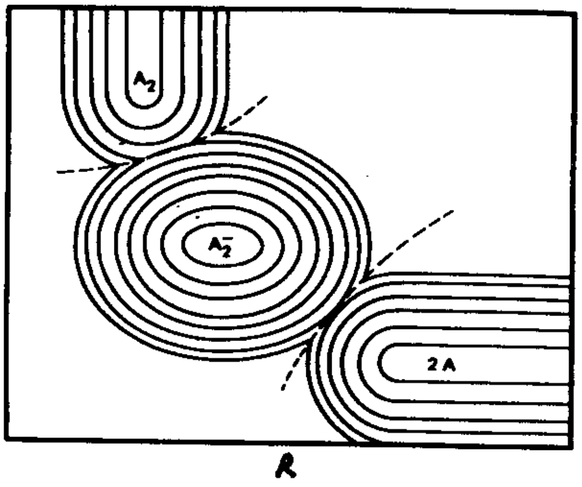
- Cold Translational and Rotational Energy Distributions





- Vibrational excitation is preserved v=0:1:2 are populated 1:0.5:(0.6±0.2)

Gadzuk Model



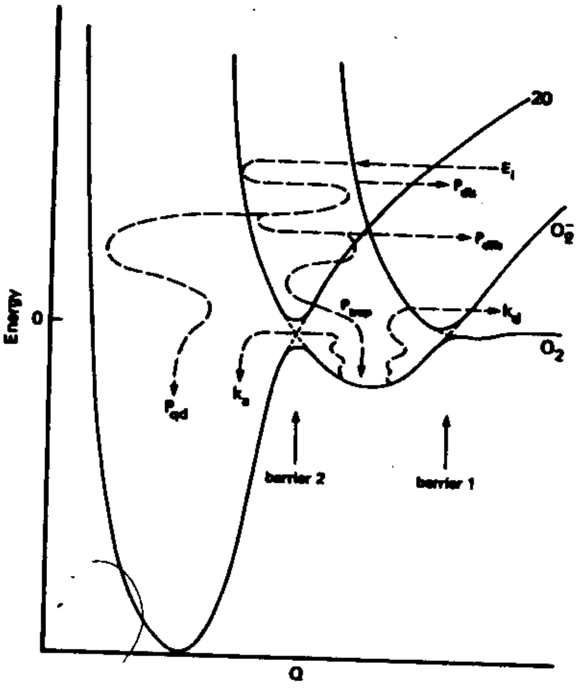
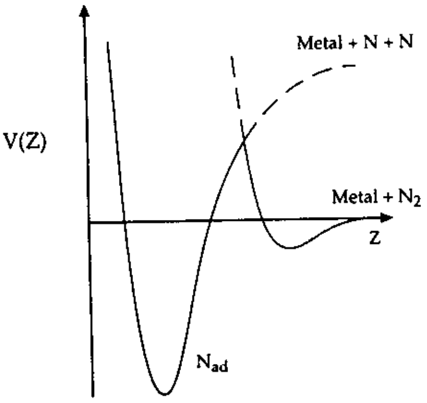


FIG. 3. Schematic 1D representation of the adiabatic PES for dissociative chemisorption of O_2 on Pt(111). Q represents some ill defined reaction coordinate. The adiabatic PES is composed of three diabatic surfaces (from right to left) O_2–Pt, O_2^-,–Pt^+, and O–Pt. Likely dynamic processes occurring on this PES are represented schematically as the dashed arrows and discussed in the text.

Conclusions

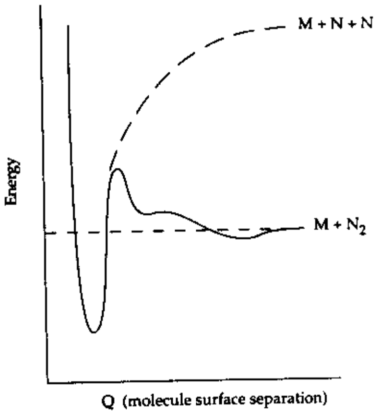
N_2 / Cu(111)

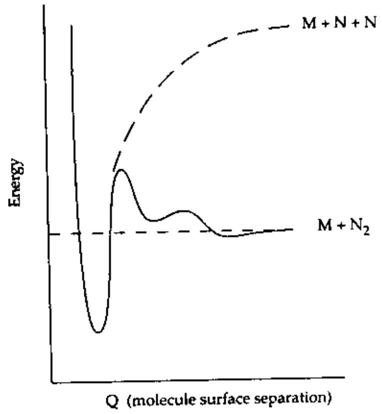
- Highly repulsive N_2-Cu potential with a dissociation barrier > 4 eV.
- Transition state has an extended N_2 bond :
  - vibration and rotation assist N_2 adsorption/desorption at Cu(111) in a similar manner as for H_2/Cu(111).



N_2 / Ru(0001)

- Desorption results in a vibrational population inversion.
- **Predict** a very sharp increase in sticking with energy, a vibrational efficacy of ~1.3 and $S < 10^{-8}$ at low energy.
- Metastable chemisorption well allows N_2 to get close to the surface, creating a PES with a high degree of curvature with the primary energy release in the N-N stretching coordinate.

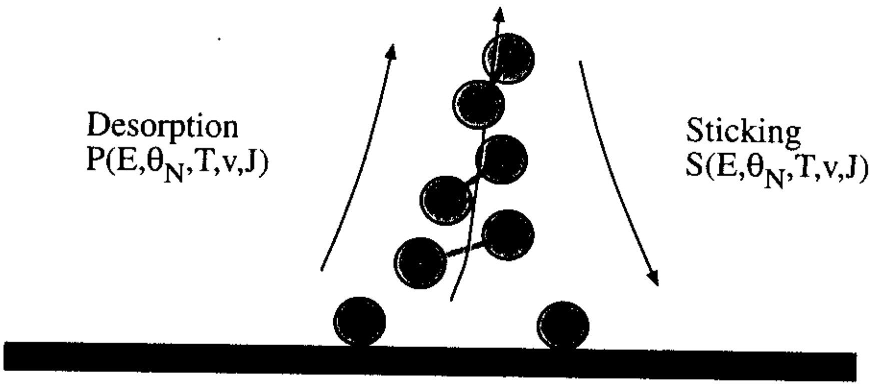




N_2 / Pd(110)

- Desorption from Pd(110) results in translationally cold N_2, consistent with trapping/accommodation in a molecular well.
- The vibrational coordinate retains its excitation -thermalisation is only partial.

Why Desorption?



- Provides fully quantum state resolved data.
- Can investigate reactions where the energy requirement is too large to study the reverse, dissociation process.
- Desorption represents a thermal sampling of the sticking function -reflects the channels which are important for thermal reaction!

  Low energy P(E) peak

  - dissociation dominated by low energy channels, not activated by translation.

  High energy P(E) peak

  - dissociation dominated by high energy channels, activated by translation.

- Detailed balance gives ro-vibrationally state resolved S above the desorption temperature, the range important for reactions.
- S(E,v,J) is free of any assumptions about the form of the sticking function.

Acknowledgements

REMPI/TOF on:

N/Cu(111)	Michael Murphy,
NH_3/Ru(0001)	John Skelly
NO+H_2/Pd(110)	Paul Samson

DFT calculations	B. Hammer Institute of Physics, Åalborg University, Denmark

Support from	EPSRC Danish Research Council