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ADRIATICO RESEARCH CONFERENCE on

LASERS IN SURFACE SCIENCE

11–15 September 2000

Miramare – Trieste, Italy

Passivation of a metal surface

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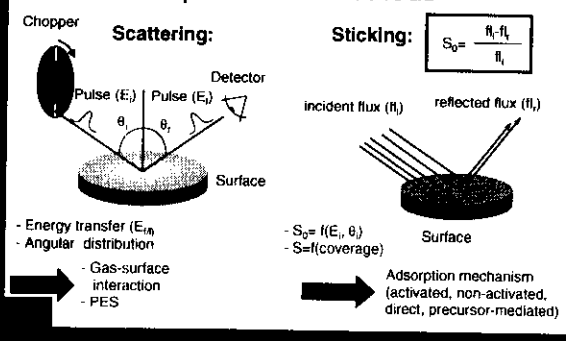
Overview

1) introduction and experimental
2) inert scattering Ar & N_2 at Ru(0001)
3) chemisorption and scattering CO / Ru(0001) & H/Ru(0001)
4) inert and reactive: NO / H/Ru(0001), rotational excitation and orientation
5) total energy calculations
6) lateral interactions and islands CO & H /Ru(0001)
7) conclusions

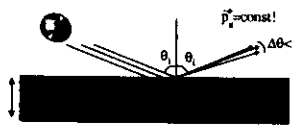
Experimental Methods



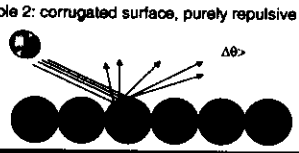
Scattering from surfaces I

How does the surface for a molecule look like?

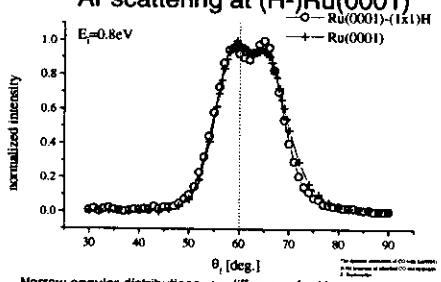
Example 1: flat surface, purely repulsive



Example 2: corrugated surface, purely repulsive

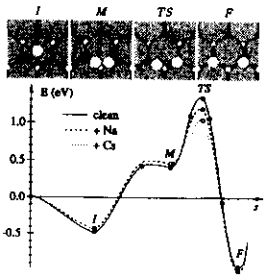


Ar scattering at (H-)Ru(0001)



Narrow angular distributions, no difference for H coverage
From: Riedmuller, Ciobica, Papageorgopoulos, Berenbak, van Santen, Kleyn, Surf. Sci. in press.

N_2 interaction with Ru(0001)

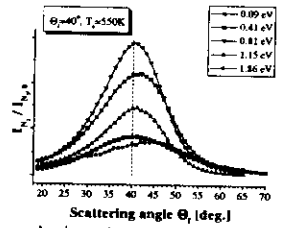


Mortensen, Hammer, Norskov, Phys. Rev. Lett. 80 (1998) 4333.

- Ru has received considerable attention in the past years as probably the only alternative to replace iron in the ammonia synthesis catalyst. The rate limiting step in ammonia synthesis is N_2 dissociation.
- In a recent theoretical study Norskov and coworkers [1] predicted the existence of a new metastable molecular precursor state to dissociation, with a 0.5 eV barrier.
- Can we see it with molecular beams?

Nitrogen scattering from Ru(0001)

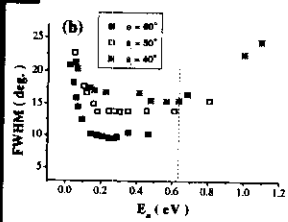
N_2 sticking negligible, Angular flux distributions:



Note the broadening at more normal incidence with high E

Papageorgopoulos, Berenbak, Verwoest, Riedmüller, Stolte, Kleyn, Chem. Phys. Lett. 305 (1999) 401.

Two scattering regimes



FWHM of the angular flux distributions with increasing incoming beam energy

- Thermal scattering at low incident energies (thermal motion of the surface important).

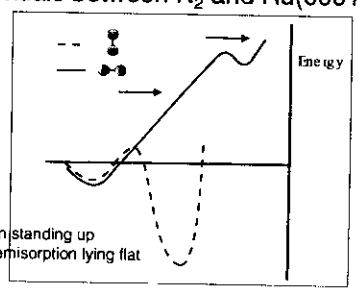
-An initial decrease in FWHM with increasing E_i due to a decrease of thermal broadening.

- Structure scattering at higher energies. Increase in width explained by an increase of surface corrugation.

- A Dual repulsive wall

Papageorgopoulos, Berenbak, Verwoest, Riedmüller, Stolte, Kleyn, Chem. Phys. Lett. 305 (1999) 401.

teraction potentials between N_2 and Ru(0001)



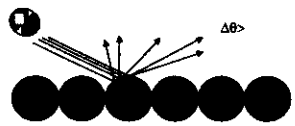
- Molecular chemisorption standing up
- Activated molecular chemisorption lying flat
- Dual repulsive wall

Papageorgopoulos, Berenbak, Verwoest, Riedmüller, Stolte, Kleyn, Chem. Phys. Lett. 305 (1999) 401.

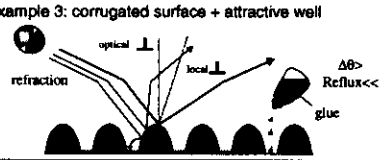
Scattering from surfaces II

How does the surface for a molecule look like?

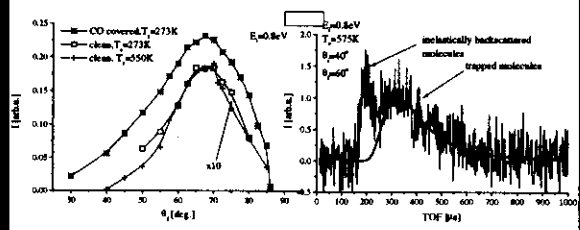
Example 2: corrugated surface, purely repulsive



Example 3: corrugated surface + attractive well



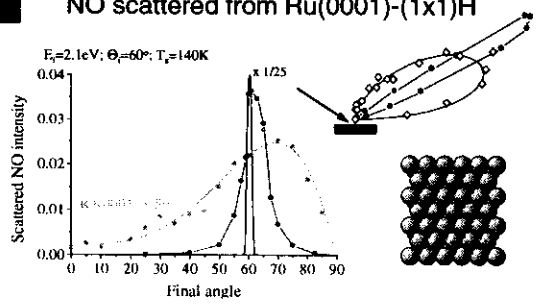
CO scattering at (CO-)Ru(0001)



Broad angular distributions, no difference for CO coverage, trapping & desorption after chemisorption

From: Riedmüller, Ciobica, Papageorgopoulos, Berenbak, van Santen, Kleyn, Surf. Sci. in press.

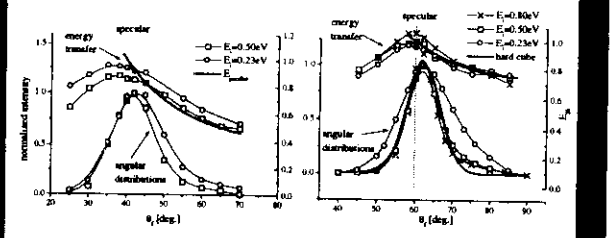
NO scattered from Ru(0001)-(1x1)H



Enhanced, sharp specular scattering

Butler, Berenbak, Stolte, Kleyn, Phys. Rev. Lett. 78 (1997) 4653.

CO scattering at H-Ru(0001)

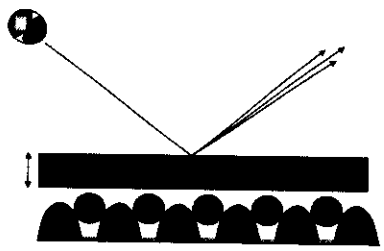


Sharp angular distributions, almost elastic scattering
From: Riedmüller, Ciobica, Papageorgopoulos, Berenbak, van Santen, Kleyn, Surf. Sci. in press.

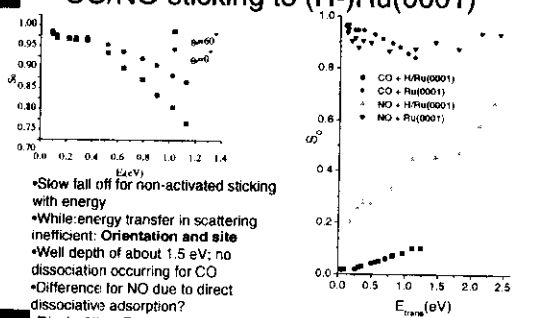
Scattering from surfaces III

How does the surface for a molecule look like?

Example 4: corrugated surface + H-passivated well



CO/NO sticking to (H-)Ru(0001)



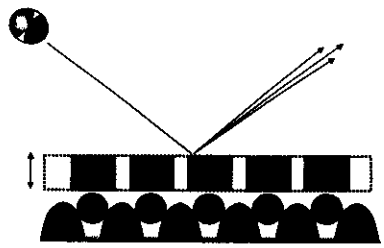
- Slow fall off for non-activated sticking with energy
- While energy transfer in scattering inefficient: **Orientation and site**
- Well depth of about 1.5 eV; no dissociation occurring for CO
- Difference for NO due to direct dissociative adsorption?

Riedmüller, Papageorgopoulos, Berenbak, Ciobica, van Santen, Kleyn

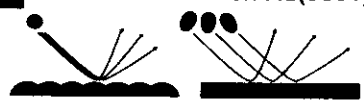
Scattering from surfaces IV

How does the surface for a molecule look like?

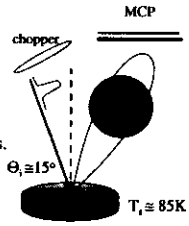
Example 5: corrugated surface + partially -passivated well



NO-REMPI on Ru(0001)-(1x1)H



Corrugation Anisotropy

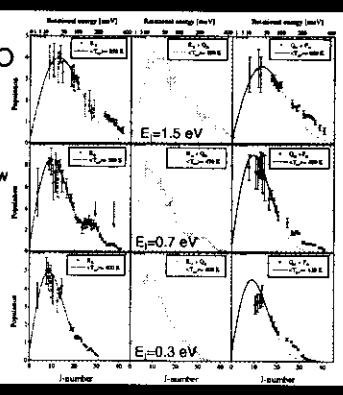


- 1+1 REMPI
- Incidence angle fixed at 15°.
- Detection over large fraction of exit angles.
- Ru(0001)-(1x1)H, $T_s \approx 85K$

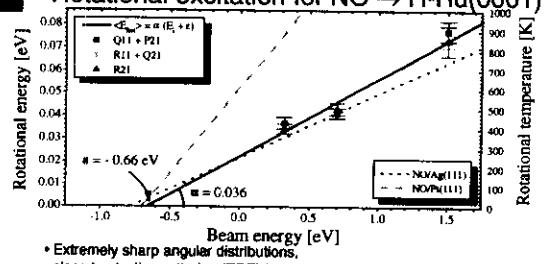
Rotational excitation for NO → H-Ru(0001)

- Rotational rainbow: inert scattering.
- Rotational distributions show anisotropy like NO/Ag(111)
- No scattering from chemisorption well.

Berenbak, Stolte, Kleyn, Auerbach, Rettner, to be publ.



Rotational excitation for NO → H-Ru(0001)

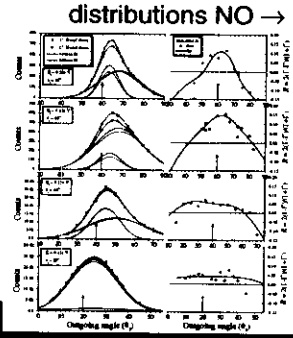


- Extremely sharp angular distributions,
- close to elastic scattering (TOF's).
- 'Inert' rotational excitation

while:

- A high reactivity of the system (K&W).
- Berenbak, Stolte, Kleyn, Auerbach, Rettner, to be publ.

Orientation dependent angular distributions NO → H-Ru(0001)



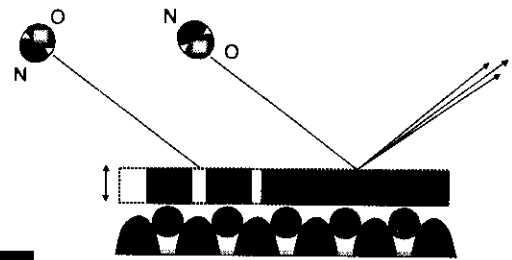
- Distributions can be fit with broad and narrow angular distribution
- N-end is broad:
  edges of well
- O-end is narrow:
  inert terrace

from:
Berenbak, Stolte, Kleyn

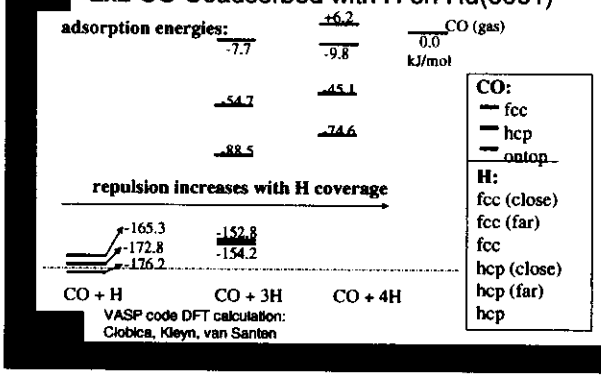
Scattering from surfaces V

How does the surface for a molecule look like?

Example 6: orientation dependent partially -passivated well

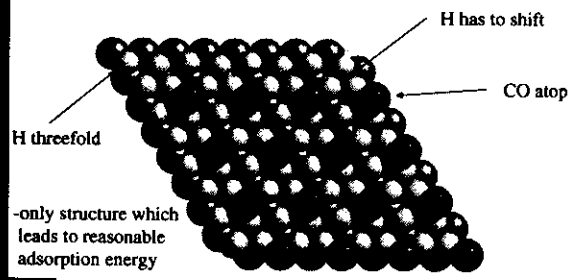


2x2 CO Coadsorbed with H on Ru(0001)



VASP code DFT calculation:
Ciobica, Kleyn, van Santen

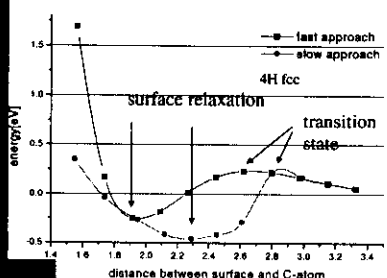
The structure:



VASP code DFT calculation: Ciobica, Frechard, Hafner, Kleyn, van Santen

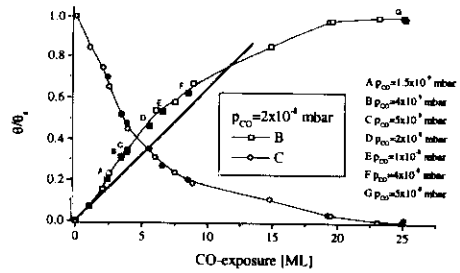
Static calculations:

-C-Ru bond fixed



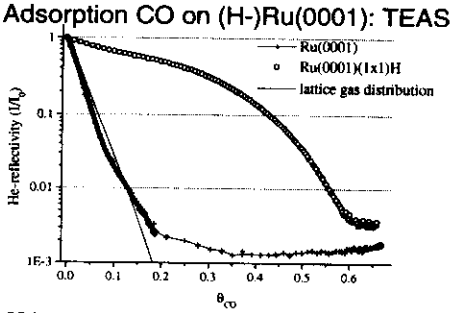
-slow surface can relax
-fast surface cannot relax
-minimum activation barrier B=0.25eV
- Ru move towards CO molecule

Co-adsorption H and CO on Ru(0001)



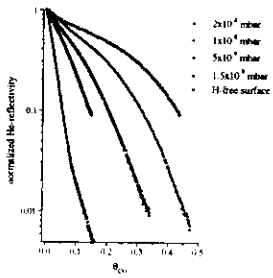
CO displaces 2 H at constant total coverage
Riedmüller et al.

Adsorption CO on (H-)Ru(0001): TEAS



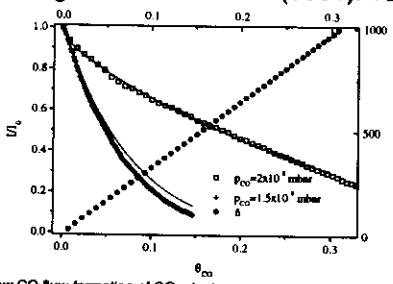
CO forms lattice gas on Ru(0001); islands on H-Ru(0001)
Riedmüller et al.

Adsorption CO on (H-)Ru(0001): TEAS



CO forms lattice gas on Ru(0001); flux dependent islands on H-Ru(0001)
Riedmüller et al.

Island growth CO on H-Ru(0001): TEAS



Low CO flux: formation of CO_2 clusters
High CO islands growing in size
Riedmöller et al.

Conclusions: scattering from (passivated) metals:

- an inert system: Ar / (H-) Ru(0001)
- activated chemisorption N_2 / Ru(0001), a dual repulsive wall
- chemisorption and scattering CO / Ru(0001): & complete passivation by H.
- inert and reactive: NO / H/Ru(0001): sticking and scattering, no corrugation but rotational excitation
- strong orientation and site dependence of interaction
- lateral interactions CO & H /Ru(0001): rapid diffusion and island growth