Part III: Theoretical Surface Science
Adsorption at Surfaces

Karsten Reuter

Lecture course: Solid State Theory
Adsorption at surfaces

(T,p)

Phase I

Phase II

Corrosion

Growth

Sensors

Heterogeneous Catalysis

Pollution Abatement

Energy Conversion
Classification of adsorbate structures I

Frenkel-Kontorova model

Coverage often measured in monolayers

1ML = (#adsorbates/surface atom)

Sub-ML vs. multilayers

Deep wells, small lateral interactions: Site-specific adsorption

Lat. interactions

Ordered overlayers

Islands / Domains
Classification of adsorbate structures II

From complex to incommensurate overlayers

Decreasing well depth / Increasing lateral interactions
Classification of adsorbate structures III

Adsorbate-substrate interaction > substrate-substrate interaction

CO-induced clock/anticlock reconstruction

Ni(100)  Ni(100) distorted c(2x2)-CO

And in extreme cases: facetting…

Monoatomic step

Multiple height step

Facetting
Physisorption: “Bonding without bonds”

H atom in front of metal surface
Image charge model

Proper QM derivation comes to equivalent result


Electrostatic energy:

\[ V_{im} = -\frac{e^2}{2} \left[ \frac{1}{|2z|} + \frac{1}{|2z + r + r'|} - \frac{1}{|2z + r|} - \frac{1}{|2z + r'|} \right] \]

Larger distances: Taylor expand in \( r/z \) (\( << 1 \)):

\[ V_{im} = -\frac{C_v}{z^3} + O\left(\frac{1}{z^4}\right) \]

\( C_v = \) van der Waals constant (~ atomic polarizability)
Physisorption vs. chemisorption

Zaremba/Kohn theory
(physisorption on jellium)
yields reasonable description
of rare-gases on noble metals

In general, however, much stronger
bonding through formation of
covalent bonds $\rightarrow$ chemisorption

Binding energy ($T = 0K$):

$$E_b = \left[ E_{\text{tot}}(\text{substrate}) - E_{\text{tot}}(\text{metal}) - E_{\text{tot}}(\text{gas}) \right]$$

Physisorption ($\sim 0.1 \text{ eV/atom}$) - Chemisorption ($\sim 2-5 \text{ eV/atom}$)
Theory of chemisorption at metals I: Effective medium theory

Consider adsorbate-surface interaction as an “embedding” into the homogeneous, averaged electron gas provided by the surface

\[ E_b \sim E_{\text{EMT}}(n) \]

i) Compute energy of adsorbate in a homogeneous density (universal curve)

ii) Compute averaged density \( n \) at the clean surface (jellium model) to get adsorption height

Achievements:
- Curves have a minimum… (no minimum for He: No vdW in EMT!)
- O has lower minimum than H: stronger binding
- O has minimum at lower \( n \): longer bond length
- more neighbours, higher \( n \): longer bonds (BOC)

Failures:
- no site specificity (jellium!)
- same bond strength for one adsorbate on all metals, as adsorbate can adjust its position freely to achieve its optimum electron density, no diffusion barrier (missing d-orbitals…)

Theory of metal chemisorption II: Newns-Anderson model

≈ a generalization of molecular orbital (MO) schemes to finite bands

free atom interaction with s-band: renormalization and broadening interaction with d-band: splitting in bonding and anti-bonding peaks clean surface

Oxygen bond strength at basal transition metal surfaces

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<th>Sc</th>
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Strong variation with element and coverage

O(2x2) | O(2x1) | 3O(2x2) | O(1x1)

hollow sites

Binding energy (eV/atom)

Theory of metal chemisorption II: Newns-Anderson model cont’d

Filling of $d$-band occupies antibonding O-M states

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Achievements:
- qualitative electronic structure at the surface
- correct trend in adsorption strength over TM series
- reactivity patterns $\rightarrow d$-band center (Hammer/Nørskov)

Failures:
- no adsorbate induced reconstructions
- no site specificity ($\rightarrow$ reactivity theory, HSAB, covalent/ionic)
- no lateral interactions
Dissociative vs. molecular adsorption I: Lennard-Jones model

Achievements:  
- qualitative trends in dissociation of simple molecules

Failures:  
- no site specificity; generalization to complex molecules
Dissociative vs. molecular adsorption II: MO picture

Achievements:
- qualitative description of electronic structure → Blyholder
- bond activation/dissociation (occupation of bonding $\sigma^*$-orbital)
- weak variation of bond strength with $d$-band filling:
  counteracting effects of antibonding $\sigma$ / bonding $\sigma^*$-orbital

Failures:
- 1D conceptual model (molecular orientation, internal substructure, level position), no site specificity
Case study for molecular adsorption: CO @ RuO$_2$(110)

HOMO “donation”: strong interaction shifts 5σ by 4eV below 1π level
LUMO “back-donation”: 2π* remains far above $E_F \rightarrow$ molecular adsorption
Adsorption dynamics: Relevance of energy dissipation

Energy transfer to substrate (phonons, electron-hole pairs) required to enable adsorption

Sticking coefficient = # of adsorbed particles / # of impinging particles

Gas: $S = S(T, \theta)$; molecular beam: $S = S(E, \Omega_i, \Omega_f, \theta)$
Hard cube model of atomic adsorption dynamics

Achievements:
- Sticking decreases with $E_{\text{kin}}$
- Increase with larger adsorbate mass (more efficient energy transfer)
- Decreasing $S(E_{\text{kin}})$ generally taken as sign for molecular (non-dissociative) adsorption
Dissociative adsorption

Dissociation opens further channel for energy transfer: Conversion of center-of-mass kinetic energy into kinetic energy of fragments relative to each other.

For light molecules like H$_2$ on heavy substrates direct energy transfer to substrate degrees of freedom negligible. Sticking entirely determined by dissociation probability.
Activated adsorption vs. non-activated adsorption

Increasing sticking due to molecules overcoming activation barrier (= taken as sign for dissociative adsorption)

H.A. Michelsen and D.J. Auerbach, J. Chem. Phys. 94, 7502 (1991);

"Elbow plot"
Case study for dissociation dynamics I: $\text{H}_2$ over Pd(100)

A. Groß, S. Wilke and M. Scheffler,

Coexistence of non-activated (minority) and activated (majority) paths...


...so why does the sticking coefficient decrease with energy?

A molecular precursor?
Quantitative sticking coefficients

~20 years for one *ab-initio* sticking coefficient

C. Rettner *et al.*, JCP 102, 4625 (1995)

**Statistics in at least six dimensions!**

\[ S = S(\theta, T) \]

**CPU cost**

*ab-initio* MD: 10 kinetic energies
x 1,000 trajectories / kinetic energy
x 1 pico sec. / trajectory
x 100 time steps / pico sec. (→ vibrations)
x 10 min. / time step

10^7 minutes
Dynamics of dissociation: “divide and conquer”


i) Compute \( V(x,y,z,d,\theta,\phi) \) \textit{ab-initio} on a grid
(~500-1000 points for 6 dimensions)

ii) Interpolate potential energy surface (PES)
- analytic functions (Morse potentials…)
- tight-binding hamiltonian
- neural networks

iii) Run MD on continuous representation of PES

Achievements: - correct statistics
- first \textit{ab-initio} \( S_\rho(T) \) for H\(_2\) dissociation
- importance of dynamic effects

Current challenges: - rigid substrate (energy dissipation,

reconstructions, steps, defects)
- PES interpolation beyond 6D
- non-adiabatic effects

(spin flips, charge transfer)
“Steering” instead of molecular precursor explains initially decreasing $S_o(E)$