

# Ultrakurze Laserpulse: wie sie helfen die Geheimnisse heterogener Katalyse zu entschlüsseln

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# Motivation: Die Bedeutung heterogener Katalyse

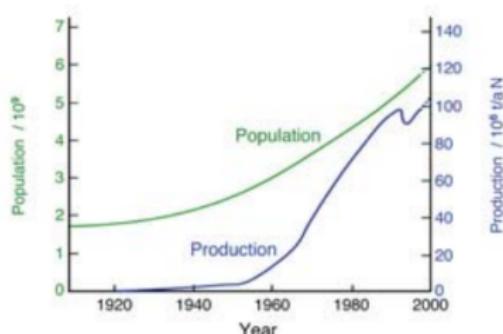
## Chemische Industrie

- Düngemittel
  - Haber-Bosch-Verfahren ( $\text{NH}_3$ )
  - Ostwald-Verfahren ( $\text{HNO}_3$ )
- Monomere
  - Ethylenoxid, Acrylsäure, Styrol

## Umwelttechnik

- Luftreinhaltung
  - Abgaskatalysatoren
  - Rauchgasentstickung
- Biokraftstoffe
- Fischer-Tropsch-Synthese

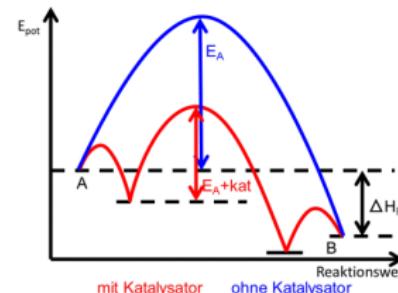
World population and ammonia production



# Heterogene Katalyse: Begriffsklärung

## Katalyse

- Aktivierungsenergie kleiner  
⇒ Reaktionen schneller
- auch wichtig: Selektivität  
(z.B. keine Durchoxidation)



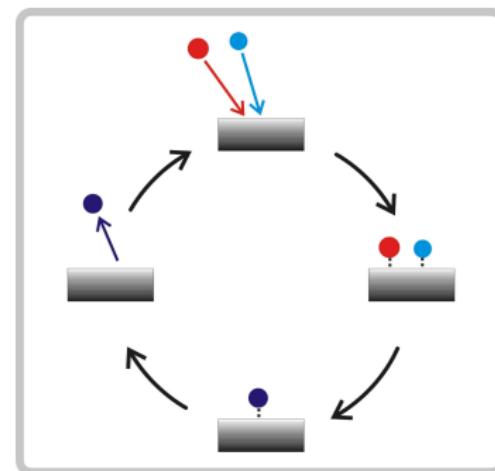
## Heterogen

- verschiedene Phasen, meist:
  - Katalysator fest
  - Reaktanden gasförmig / flüssig

# Prinzipieller Mechanismus heterogener Katalyse

z.B. Langmuir-Hinshelwood

- ① Adsorption Edukte
  - Schwächung von Bindungen
  - ggf. Dissoziation
- ② Oberflächendiffusion
- ③ Reaktion
- ④ Desorption Produkt(e)



Aber weiterhin viele ungeklärte Fragen

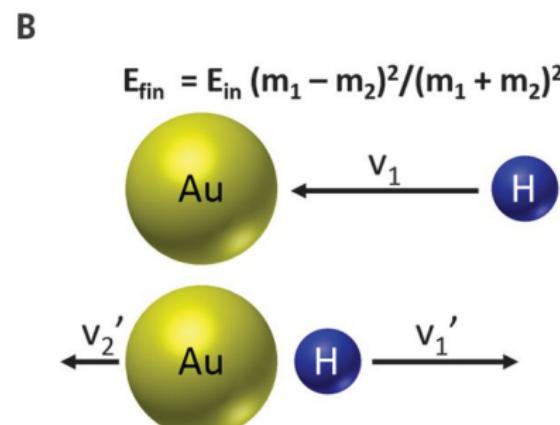
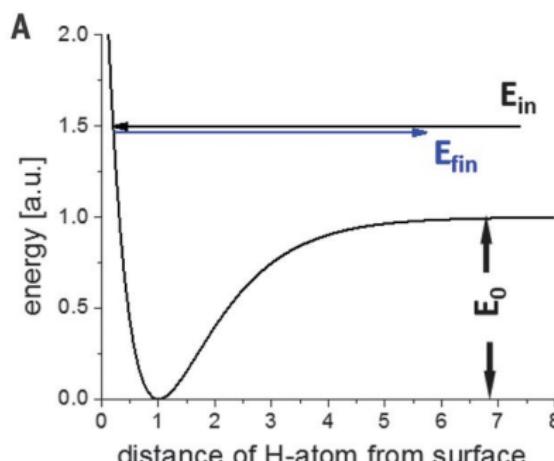
⇒ Grundlagenforschung an Modellsystemen nötig

- besonders für Metall-Adsorbat-Bindung viele Wissenslücken

# Wie binden Adsorbate an Metalle?

Protonen "kleben" an Metalloberflächen

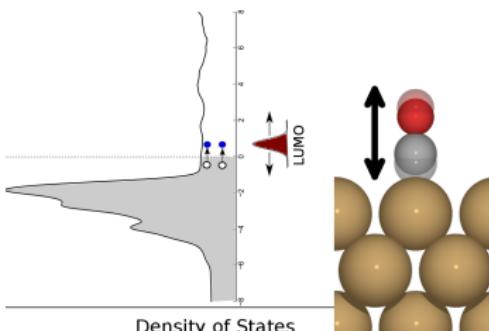
- Aber, einfaches Stoßmodell: 98% Energie erhalten
- was fehlt?  $\Rightarrow$  Elektronische Reibung!



# Elektronische Reibung in Metall-Adsorbat-Systemen

## Was ist Elektronische Reibung?

- Wechselwirkung zwischen Adsorbat und Elektronengas
- Ursache: fehlende Bandlücke in Metallen  
⇒ Anregung von Elektron-Loch-Paaren sehr leicht



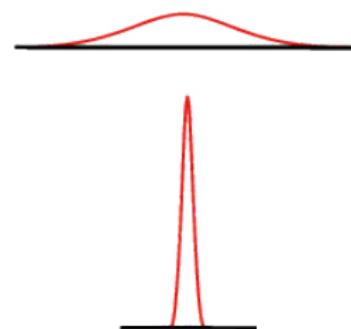
## Was bewirkt elektronische Reibung?

- Abremsen von Adsorbaten
- starke Dämpfung von Vibrationen  
⇒ Lebenszeit  $\sim$  ns
- umgekehrt, bei hohen Temp.:  
Fluktuationen ⇒ Anregung

# Ultrakurze Laserpulse

## Einteilung

- Pikosekundenlaser
  - $1 \text{ ps} = 10^{-12} \text{ s}$
  - ab  $\approx 1 \text{ ps}$  Pulsdauer
- Femtosekundenlaser
  - $1 \text{ fs} = 10^{-15} \text{ s}$
  - typische Pulsdauer: 50 - 200 fs
- beide: Spitzenleistung  $\gg$  cw-Laser



## Erforschung elektronischer Reibung

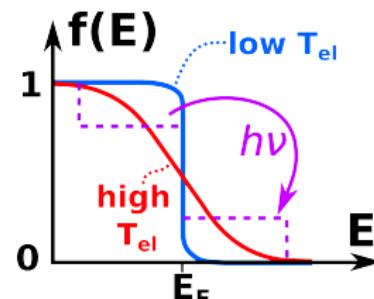
- Warum reichen ps-Laser nicht?
- Was macht fs-Laser besonders?

?

# Wirkung von optischen fs-Lasern auf Metalle

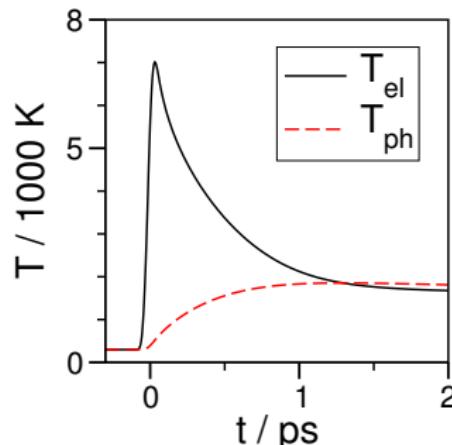
## Wie wird Energiepuls aufgenommen?

- Nur Elektronen des Metalls absorbieren  
(Und nur teilweise, Rest: Reflektion)
- Elektronen thermalisieren in 10-100 fs  
⇒ danach Fermi-Dirac-Verteilung  $f(E)$



## Wie verteilt sich die Energie im Metall?

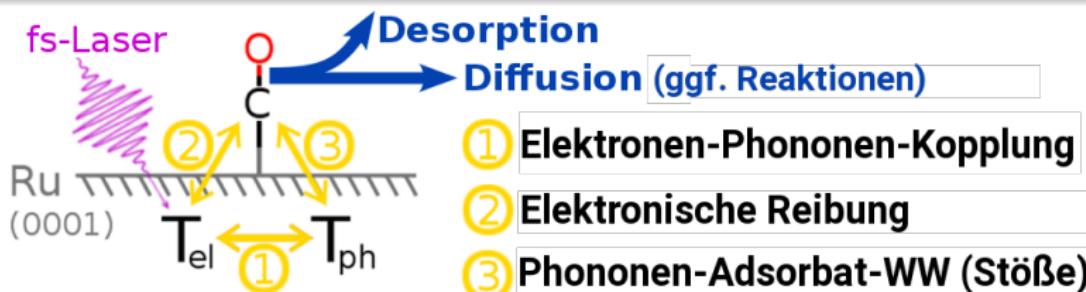
- ① Diffusion heißer  $e^- \Rightarrow$  Wärmetransport
- ② Kopplung zwischen Elektronen und Gitterschwingungen (sog. Phononen)
  - Dauer: ps ⇒ **2 versch. Temperaturen**
  - anfangs alle Energie in  $e^-$ -System
  - da  $e^-$  allein geringe Wärmekapazität:  
⇒ **sehr hohe  $e^-$ -Temperatur  $T_{el} > 5000$  K**



# Indirekte Wirkung des fs-Lasers auf Adsorbat

Metall im 2-Temperatur-Zustand wechselwirkt mit Adsorbat

- ① über Elektron-Loch-Paare (e-h-Paare)
  - elektronische Reibung (Dissipation)
  - Anregungen durch heiße e-h-Paare (Fluktuation)  
⇒ verursachen Zufallskräfte (daher sog. Langevin-Dynamik)
- ② über Stöße mit Phononen

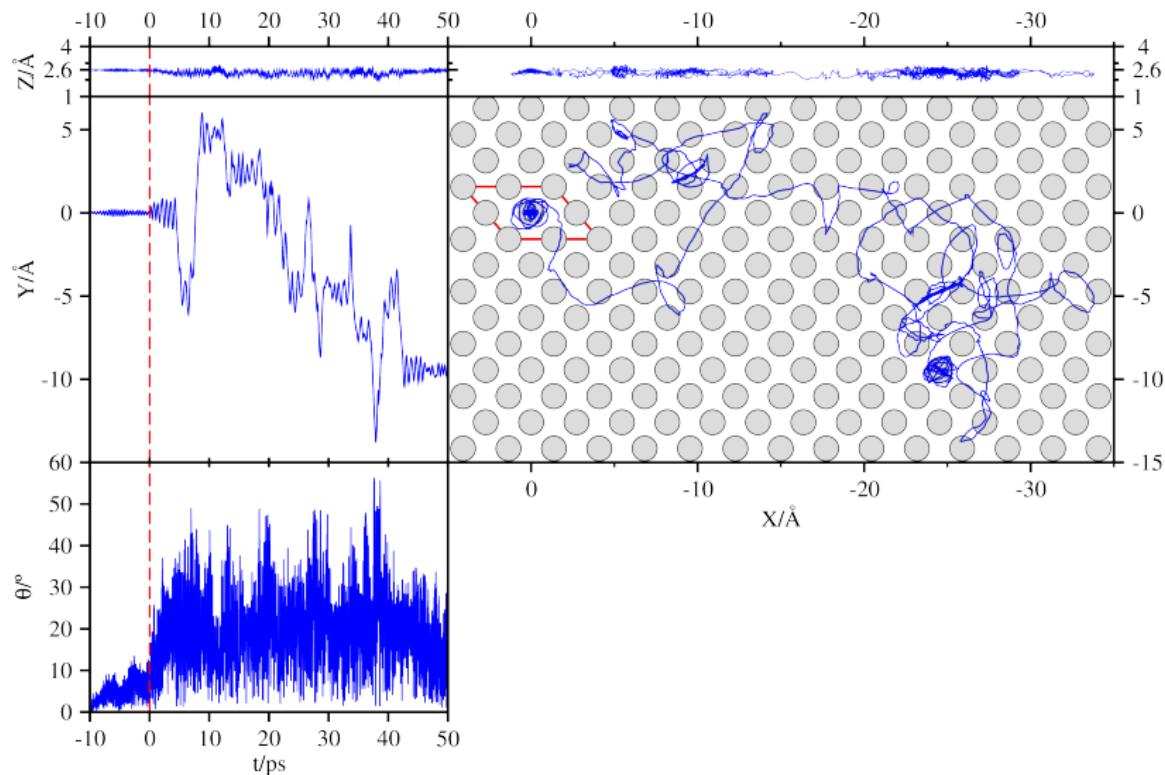


Im Folgenden, zwei verschiedene Modelle:

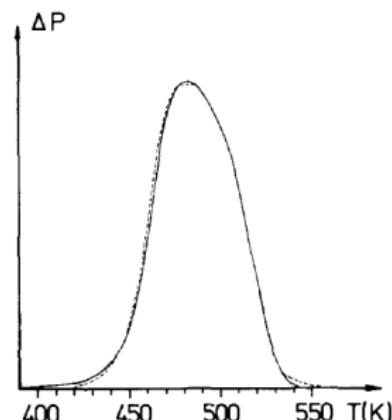
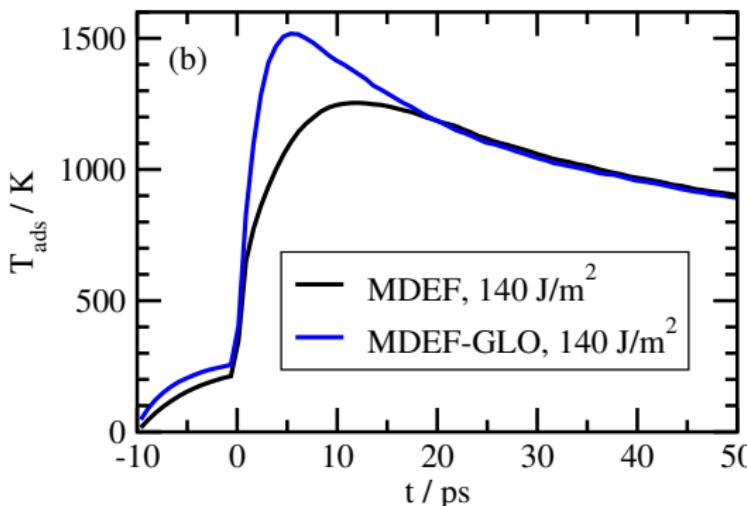
ohne (3): **MDEF**

mit (3): **MDEF-GLO**

# Beispiel CO auf Ru - Diffusion nach Laseranregung



# Beispiel CO auf Ru - Adsorbattemperatur



## simulierte Adsorbattemperatur $T_{\text{ads}}$

- über je 20000 Trajektorien gemittelt
- Vorsicht: keine "richtige" Temperatur (Verteilung der Energie evtl. anders)

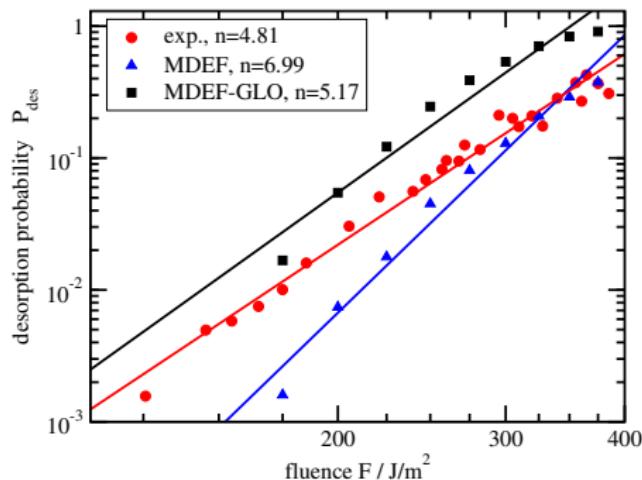
## TPD-Spektrum

- Desorption bereits ab 450K erwartet

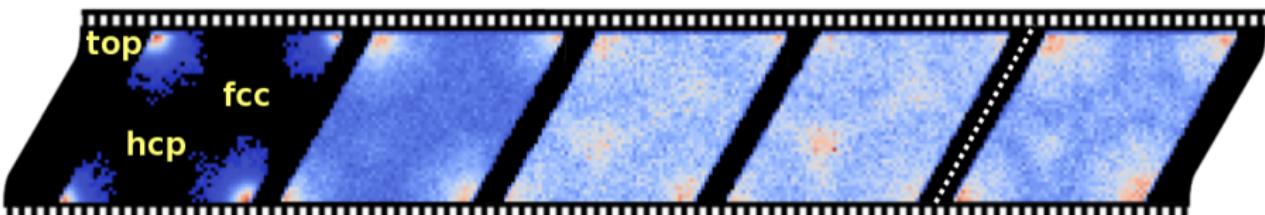
# Beispiel CO auf Ru - Lasergetriebene Desorption

## Desorption vs. Laserfluenz (doppelt logarithmisch)

- folgt grob Potenzgesetz  
 $P_{\text{des}} = A \cdot F^n$
- MDEF-GLO: Werte zu hoch, dafür aber fast korrektes  $n$
- MDEF:  $n$  stark abweichend  
⇒ überschätzt Nicht-Linearität

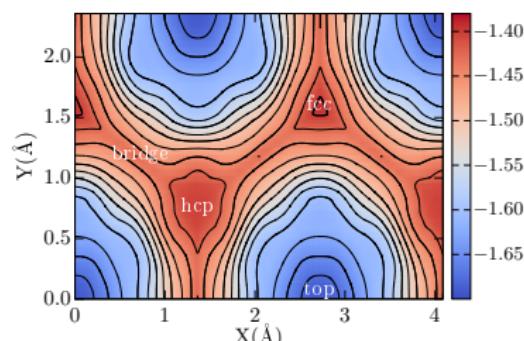


# Beispiel CO auf Ru - “dynamischer Fallen-Effekt”



## Überraschende Muster in XY-Ebene

- vor Laser: alle Moleküle auf **top**
- nach 5 ps: **hcp**-Stelle bevorzugt obwohl lokales Maximum!  
⇒ “dynamical trapping”
- 30 ps: wieder abgekühlt  
⇒ **top**-Stelle wieder favorisiert



# Zusammenfassung und Ausblick

## Zusammenfassung

- Grundlagenforschung um Katalyse tiefer zu verstehen
- Adsorbate auf Metallen unterliegen elektronischer Reibung
- fs-Laserpulse regen zunächst nur Elektronen an
- hohe Elektronentemperaturen  $T_{el} \Rightarrow$  Adsorbatdynamik

## Ausblick

- andere Systeme, z.B. CO/Cu, NO/Au, H<sub>2</sub>/D<sub>2</sub>/Ru
- Verbesserungen der Methoden, z.B. Reibung, 2T-Modell
- komplexeres Modell, z.B. mehrere Adsorbatmoleküle

# Danksagung

Vielen Dank...

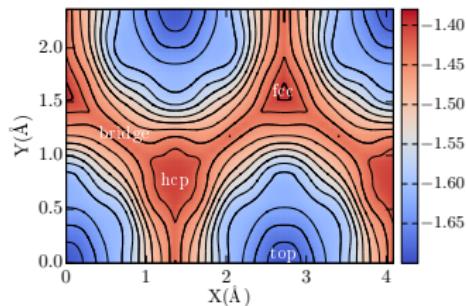
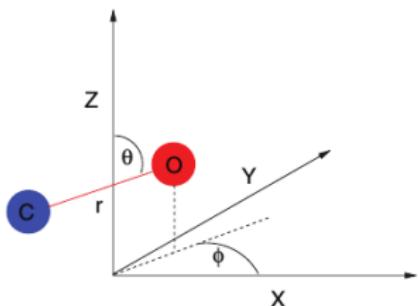
- ... für die wunderbare Betreuung, sowohl fachlich als auch menschlich, an Prof. Peter Saalfrank!
- ... für die tolle Arbeitsatmosphäre an die gesamte Arbeitsgruppe, insbesondere Büro D2.04/05!



Und euch vielen Dank für die Aufmerksamkeit!

# Further specific motivation for investigating CO/Ru

Füchsel *et al.*, JChemPhys 2014



Important prior theory work was done at our group

Füchsel *et al.*, JChemPhys 2014

- Development of a potential energy surface (PES)

- from over 90 000 DFT points!
- all 6 dimensions of the adsorbate
- very fast because preconstructed

⇒ **enables large-scale dynamics!**

# Details of the time-resolved x-ray experiment

Dell'Angela *et al.*, *Science* 2013 (experimental part by Nilsson group, SLAC/LCLS, Stanford)

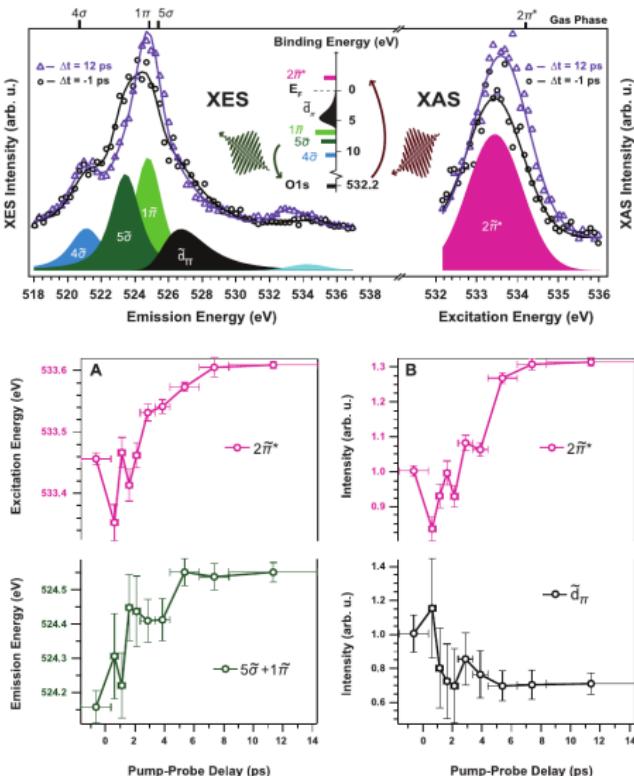
## What was done?

- pump: *vis-fs-laser*
- probe: x-ray free  $e^-$  laser
  - K-edge of O-atom

## What is observed?

- orbital density of states at O
- energies shift towards gas-phase values of CO
- intensities change
  - $2\tilde{\pi}^*$   $\Rightarrow$  increase by  $\sim 30\%$
  - $\tilde{d}_{\pi}$   $\Rightarrow$  decrease by  $\sim 30\%$
  - participant peak appears

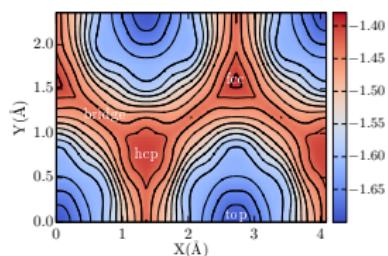
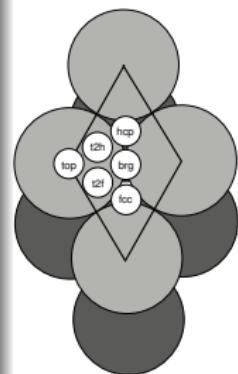
$\Rightarrow$  physisorbed precursor(?)



# More facts about the potential energy surface (PES)

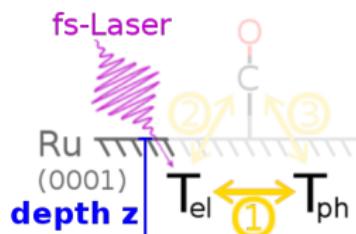
## How was it constructed?

- GGA-level (RPBE) with VdW-correction (D2)
- (2x2) cell with 1 CO  $\Rightarrow$  14 atoms, 0.25 ML coverage
  - all 6 dimensions of adsorbate  $\Rightarrow$  surface atoms frozen
- interpolation with cubic splines and corrugation reducing procedure (CRP)
  - atomic potentials temporarily subtracted  
 $\Rightarrow$  smoother intermittent potential, interpolates better
- slightly newer PES:  $C_{3v}$ - instead of  $C_{6v}$ -symmetry
  - differences between hcp and fcc sites not neglected

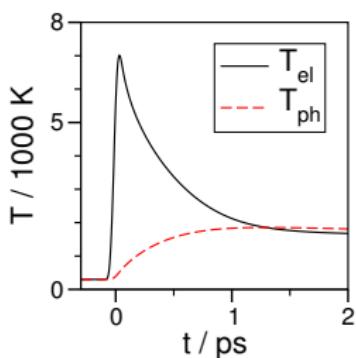


# Two-temperature model (TTM)

Two coupled heat diffusion equations



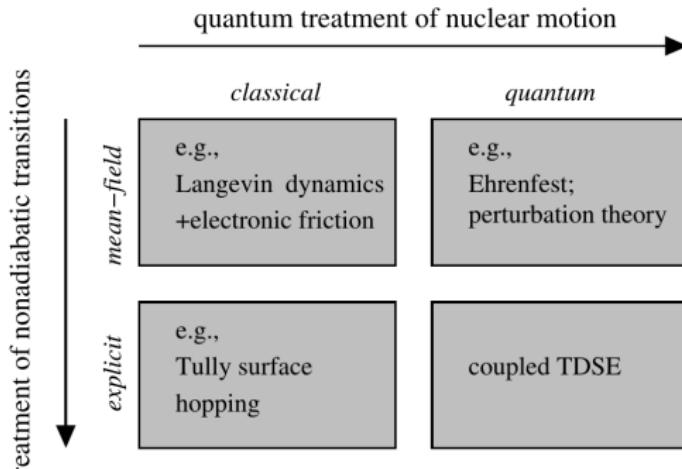
$$\begin{aligned} & \text{Heat diffusion along z-direction} \\ C_{\text{el}} \frac{\partial T_{\text{el}}}{\partial t} = & \underbrace{\frac{\partial}{\partial z} \kappa \frac{\partial}{\partial z} T_{\text{el}}}_{\text{Heating/cooling rate at depth } z} - g(T_{\text{el}} - T_{\text{ph}}) + S(z, t), \\ & \text{Electron-phonon coupling} \\ C_{\text{ph}} \frac{\partial T_{\text{ph}}}{\partial t} = & g(T_{\text{el}} - T_{\text{ph}}). \end{aligned}$$



Original TTM (Anisimov *et al.*, SovPhys-JETP 1974)

- $T_{\text{el}}$  and  $T_{\text{ph}}$  as  $f(z, t)$  from laser/material properties
  - $C_{\text{el}}$  and  $C_{\text{ph}}$   $\Rightarrow$  heat capacities
  - $\kappa = \kappa_0 \frac{T_{\text{el}}}{T_{\text{ph}}}$   $\Rightarrow$  electron heat conductivity
  - $g$   $\Rightarrow$  electron-phonon coupling constant
  - $S(z, t)$   $\Rightarrow$  depends on pulse shape,  $\lambda$ , fluence  $F$

# Different approaches to non-adiabatic coupling

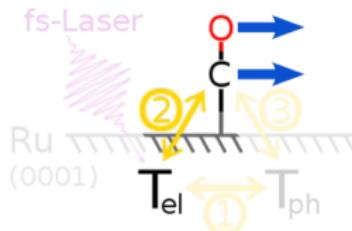


## Langevin dynamics + electronic friction

- fastest method  $\Rightarrow$  suited for multi-dimensional dynamics
- good approximation for weak non-adiabatic coupling

# The Langevin equation

A stochastic differential equation



$$m_k \frac{d^2 \underline{r}_k}{dt^2} = \underbrace{-\nabla_k V(\underline{r}_1, \underline{r}_2)}_{\text{Force on Atom } k} - \underbrace{\eta_{el,k}(\underline{r}_k) \frac{d\underline{r}_k}{dt}}_{\text{Friction force slows movement}} + \underbrace{R_{el,k}(t)}_{\text{Random force from e-h pairs}}$$

## Langevin equation within IAA (independent atom approx.)

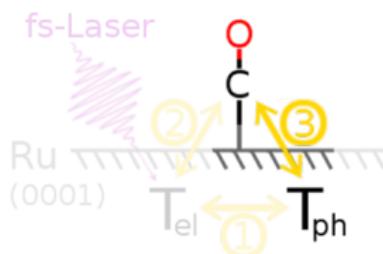
- friction coefficient of Atom  $k$ :  $\eta_{el,k}(\underline{r}_k) \Rightarrow$  dissipation
  - derived from local density friction approximation (LDFA)  
⇒ individual atom (again IAA) in free electron gas
  - $\eta_{el,k}(\underline{r}_k)$  dependent on electron density of bare surface
- random force  $R_{el,k}(t) \Rightarrow$  fluctuation
  - Gaussian white noise
  - describes excitation by hot electron-hole pairs
  - proportional to:  $\eta_{el,k}(\underline{r}_k)$  and  $T_{el}(t)$

# Generalized Langevin Oscillator

$$m_s \frac{d^2 \underline{r}_s}{dt^2} = -\underbrace{\nabla_s V(\underline{r}_1 - \underline{r}_s, \underline{r}_2 - \underline{r}_s)}_{\text{Force due to PES}} - m_s \underline{\underline{\Omega}}^2 \underline{r}_s + m_s \underline{\underline{\Lambda}}_{gs} \underline{r}_g$$

Harmonic oscillator      Coupling to ghost oscillator

coupled via potential gradient  
(i.e. collisions "nudge" surface)



**Surface oscillator**  
 $\underline{r}_s$

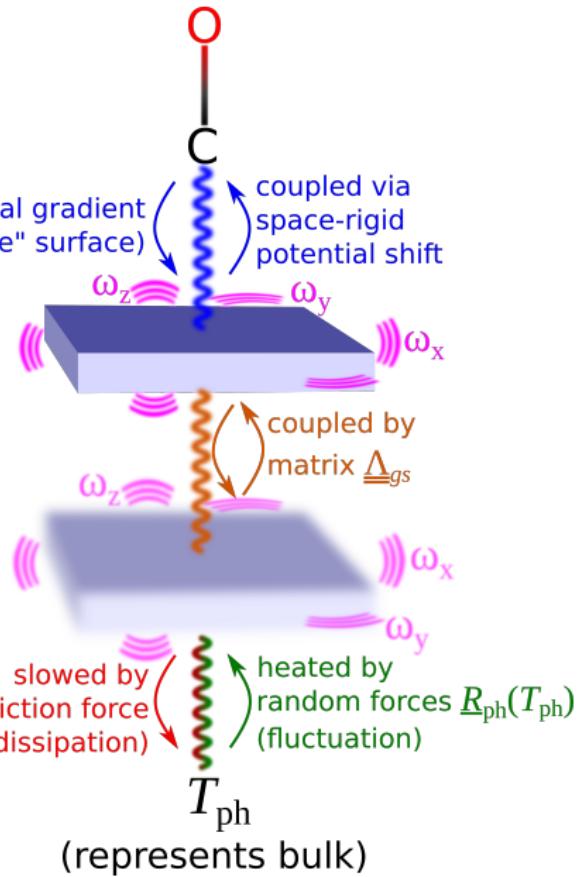
both oscillate in the  
3 dimensions x, y, z

**Ghost oscillator**

$\underline{r}_g$

$$m_s \frac{d^2 \underline{r}_g}{dt^2} = -m_s \underline{\underline{\Omega}}^2 \underline{r}_g + m_s \underline{\underline{\Lambda}}_{gs} \underline{r}_s - \eta_{ph} \frac{dr_g}{dt} + R_{ph}(T_{ph})$$

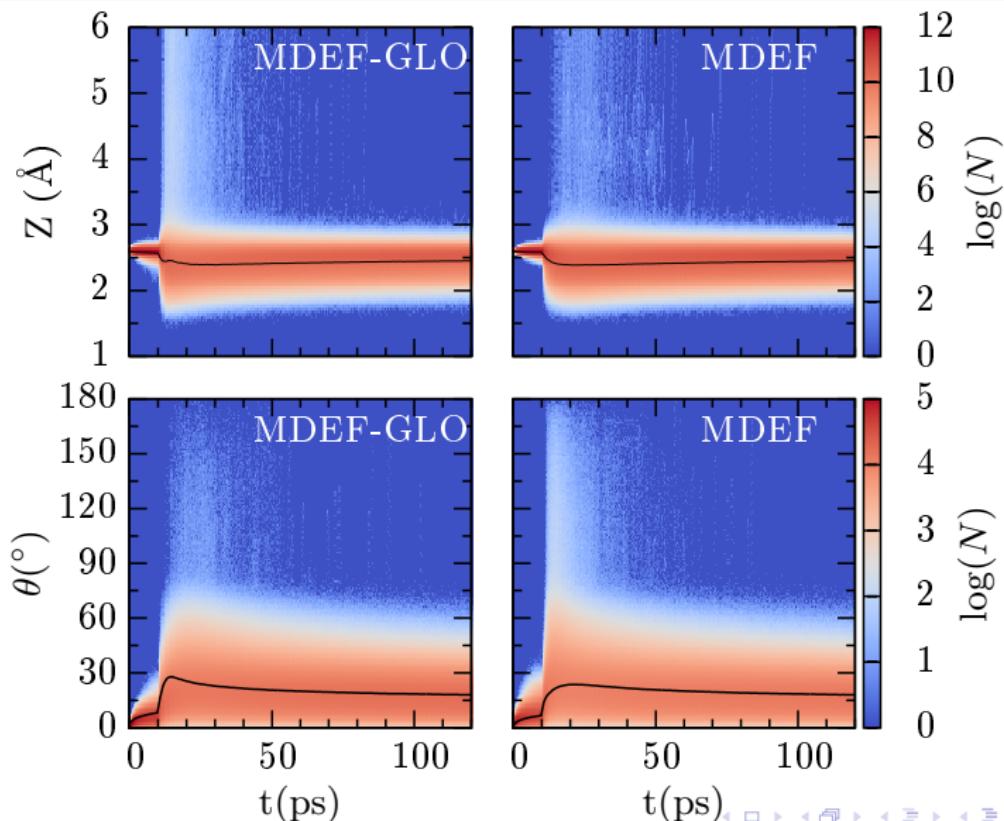
Harmonic oscillator      Coupling to surface oscillator      Friction force      Random forces



# Summary of models and methods

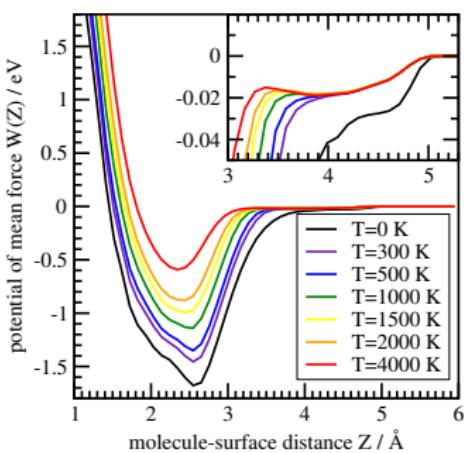
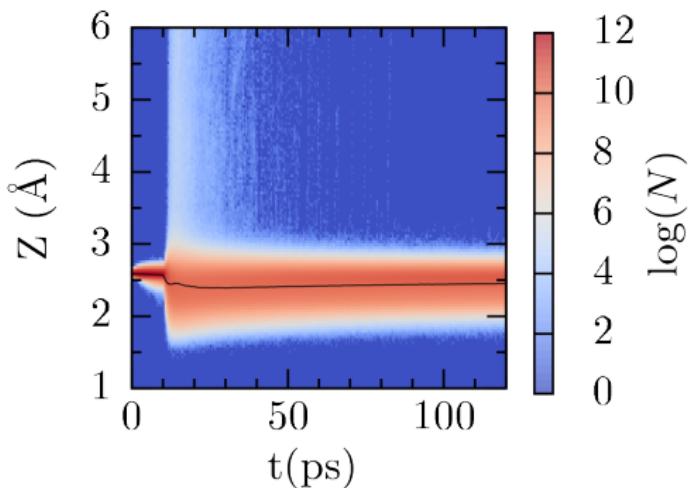


# Heating of DOFs $Z$ and $\theta$



# No population of physisorbed state in our dynamics

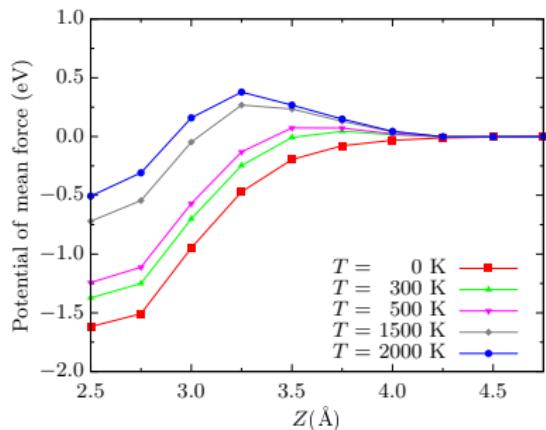
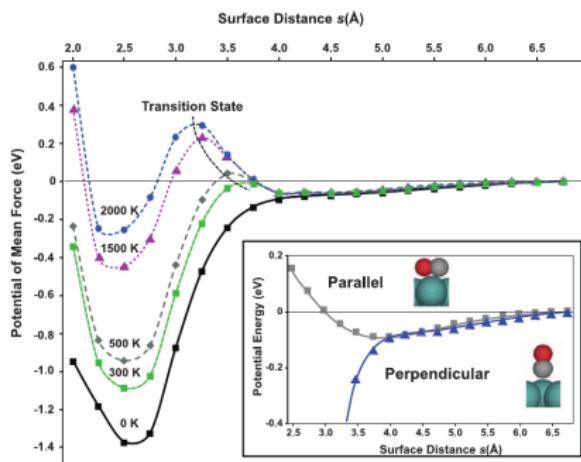
As is to be expected from negligible barrier in potential of mean force (PMF)



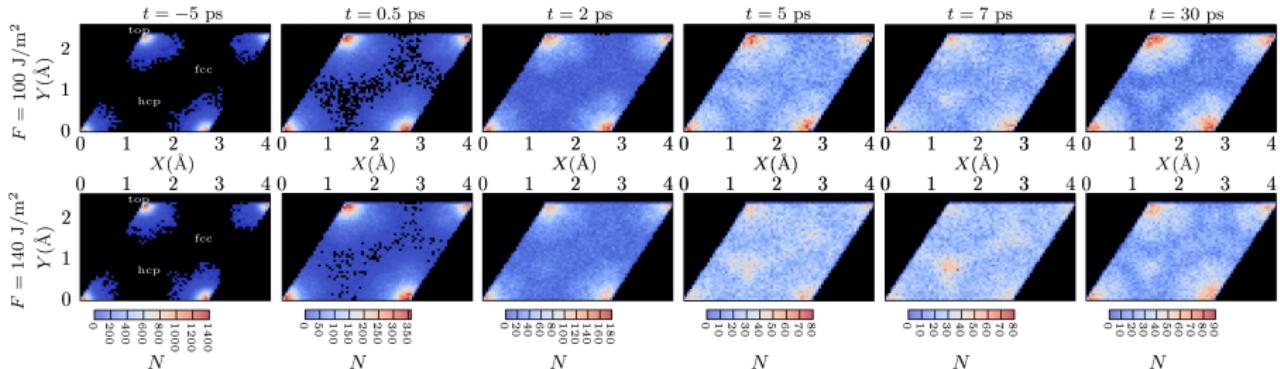
# Why are the entropic barriers of the PMFs so different?

Because separability assumption fails clearly

- if introduced for our PMF  $\Rightarrow$  barrier of similar height!
- expectable, because  $X/Y$  and  $\theta$  strongly coupled

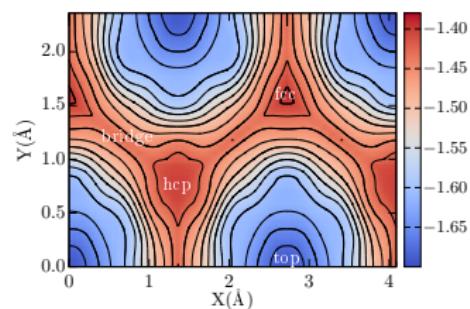


# Dynamical trapping: alternative/additional explanation?

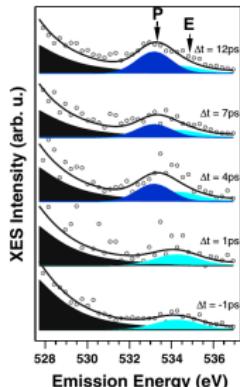
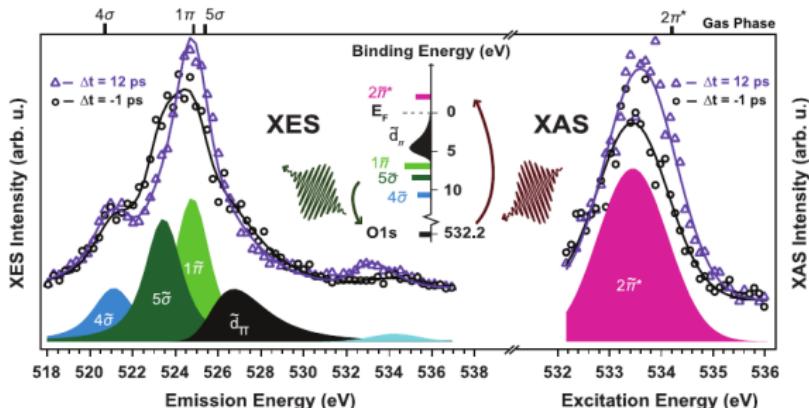


## Surprising patterns in XY-distribution

- preference of **hcp-site** after 5-7 ps, despite it being a local maximum!  
⇒ **dynamical trapping** (cf. 30 ps)
- effect dependent on fluence  
⇒ consistent with experiment  
(weaker “precursor”-signal for lower fluence)



# Is there a physisorbed precursor state nevertheless?



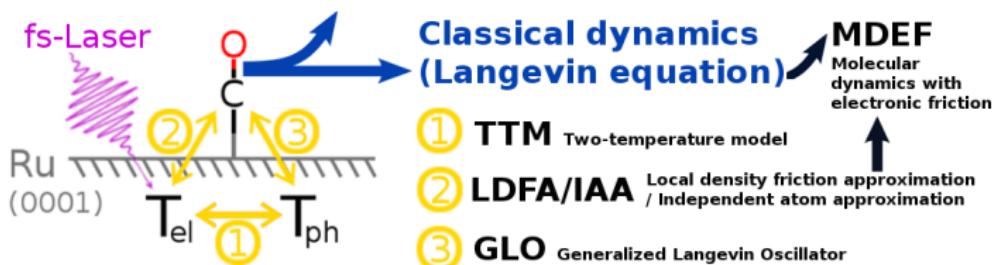
Dynamical trapping can't explain all observations

- XAS of hcp-site:  $2\pi^*$ -intensity not increased (computed by Christopher)
- participator peak not explained by any XY-redistributions  
⇒ Existence of physisorbed state very likely
- but nevertheless not stable for Ru(2x2):CO models  
⇒ probably stabilized by CO-CO interactions

# Summary

## What was done?

- 6D Langevin dynamics of CO @ Ru(0001)
  - electronic friction and excitation by hot e-h-pairs (via LDFA/IAA)
  - substrate motion (via GLO)
  - based on ab-initio potential and first-principles, no “free parameters”



## What could be learned?

- detailed time- and space-resolved insight
- physisorbed precursor state not stable in current model

# Outlook

What can be done in the future?

## On the CO/Ru-system

- better TTM, with accurate  $\kappa(T_{\text{el}}, T_{\text{ph}})$  and  $g(T_{\text{el}}, T_{\text{ph}})$  (e-e-scattering)
- better friction model, e. g. LDFA with Atoms in Molecules (AIM)
- use AIMDEF to revisit short timescales of phonon-adsorbate coupling predicted by GLO
- include CO-CO-interactions,  
e. g. via tailored FF for electrostatic and VdW-interactions  
⇒ also enables simulation of other coverages

## MDEF/GLO and AIMDEF on other systems

e.g. NO/Au(111), H<sub>2</sub>/Au(111) etc.