

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

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Motivation: Die Bedeutung heterogener Katalyse

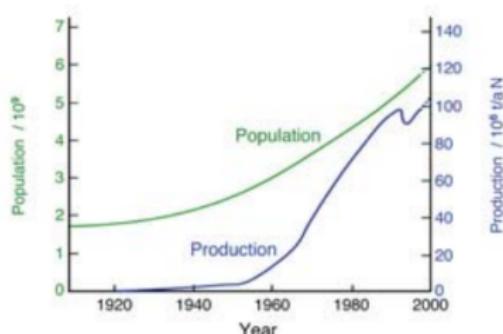
Chemische Industrie

- Düngemittel
 - Haber-Bosch-Verfahren (NH_3)
 - Ostwald-Verfahren (HNO_3)
- Monomere
 - Ethylenoxid, Acrylsäure, Styrol

Umwelttechnik

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

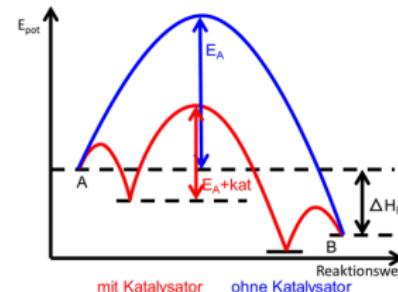
World population and ammonia production



Heterogene Katalyse: Begriffsklärung

Katalyse

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



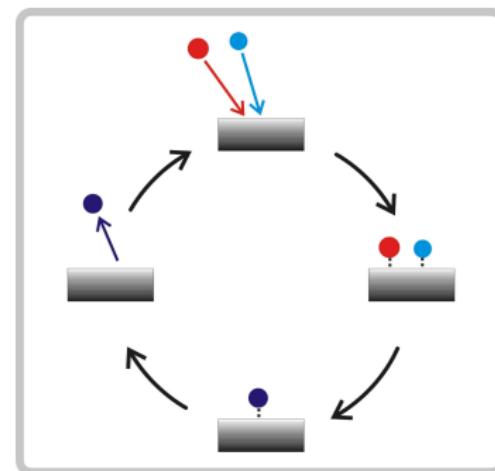
Heterogen

- 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

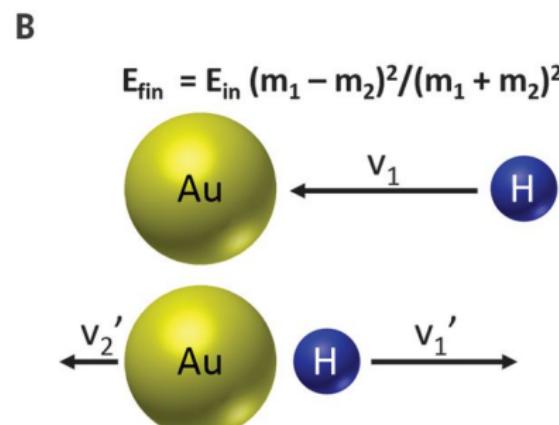
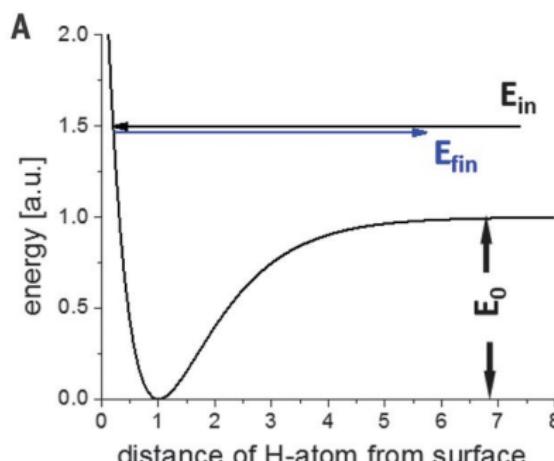
⇒ Grundlagenforschung an Modellsystemen nötig

- besonders für Metall-Adsorbat-Bindung viele Wissenslücken

Wie binden Adsorbate an Metalle?

Protonen "kleben" an Metalloberflächen

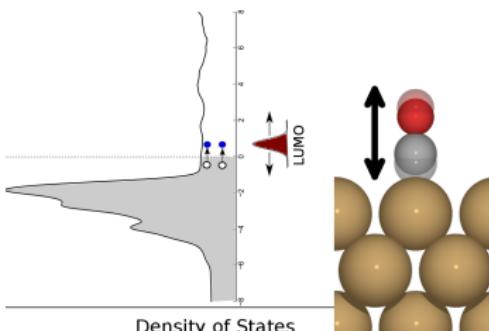
- Aber, einfaches Stoßmodell: 98% Energie erhalten
- was fehlt? \Rightarrow Elektronische Reibung!



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



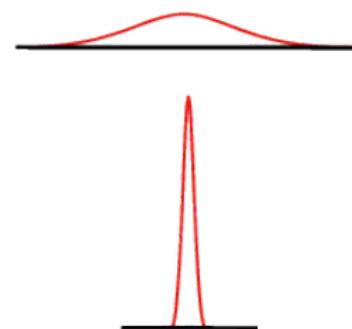
Was bewirkt elektronische Reibung?

- 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

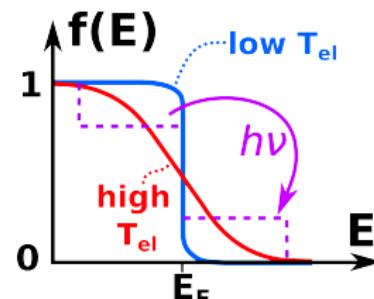
- Warum reichen ps-Laser nicht?
- Was macht fs-Laser besonders?

?

Wirkung von optischen fs-Lasern auf Metalle

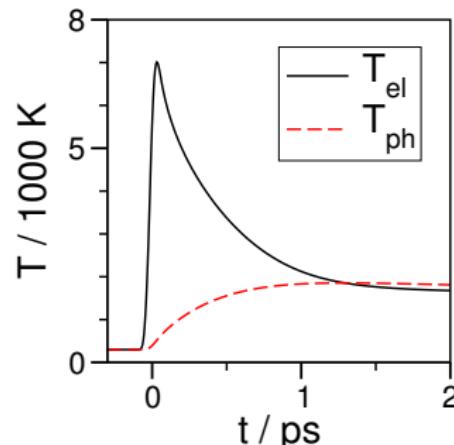
Wie wird Energiepuls aufgenommen?

- 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?

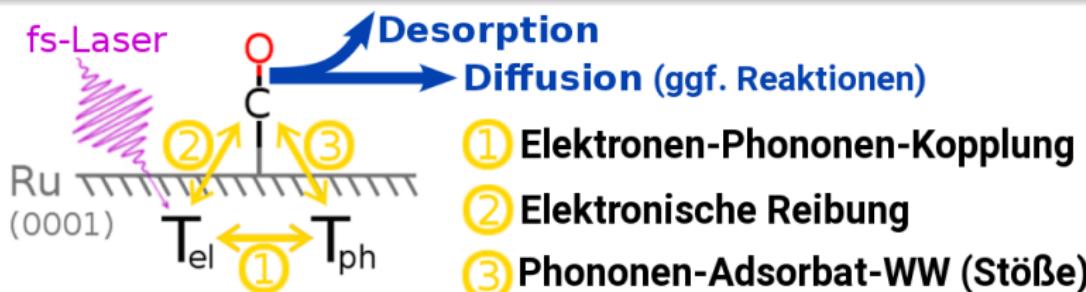
- ① Diffusion heißer $e^- \Rightarrow$ Wärmetransport
- ② Kopplung zwischen Elektronen und Gitterschwingungen (sog. Phononen)
 - Dauer: ps ⇒ **2 versch. Temperaturen**
 - anfangs alle Energie in e^- -System
 - da e^- allein geringe Wärmekapazität:
⇒ **sehr hohe e^- -Temperatur $T_{el} > 5000$ K**



Indirekte Wirkung des fs-Lasers auf Adsorbat

Metall im 2-Temperatur-Zustand wechselwirkt mit Adsorbat

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

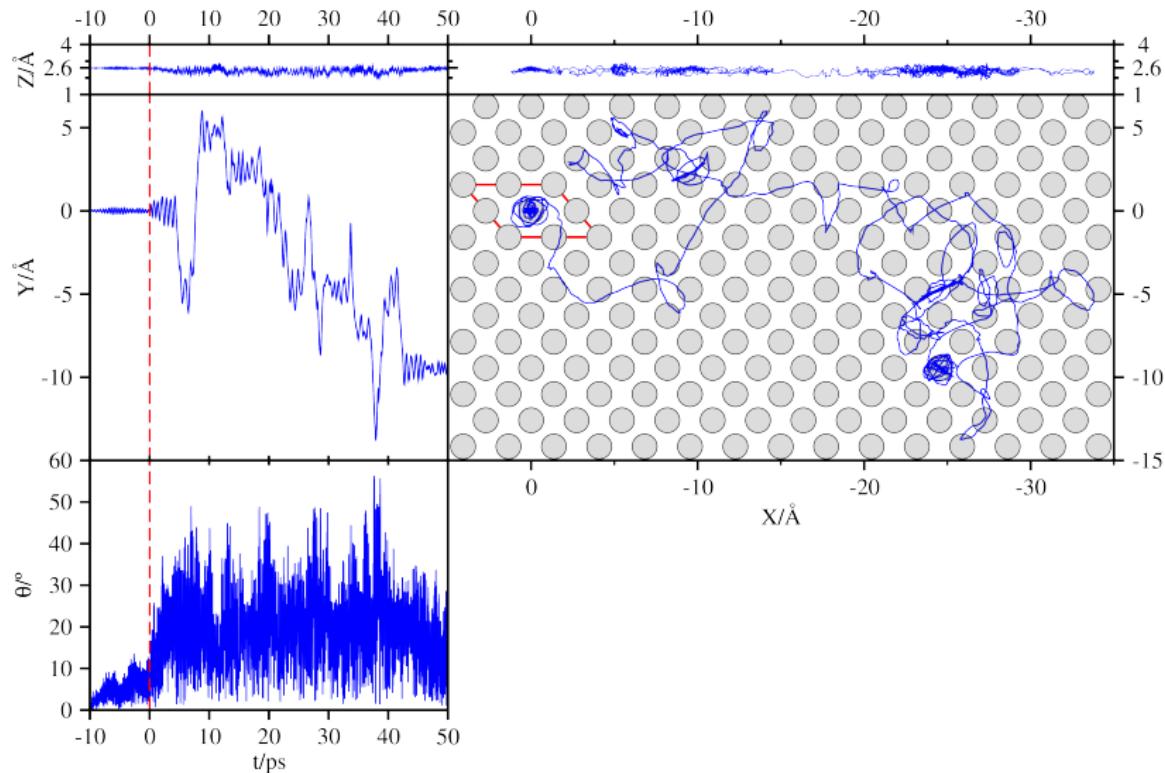


Im Folgenden, zwei verschiedene Modelle:

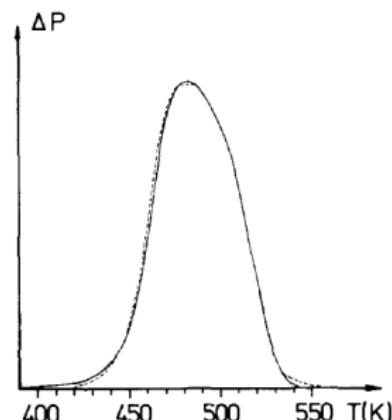
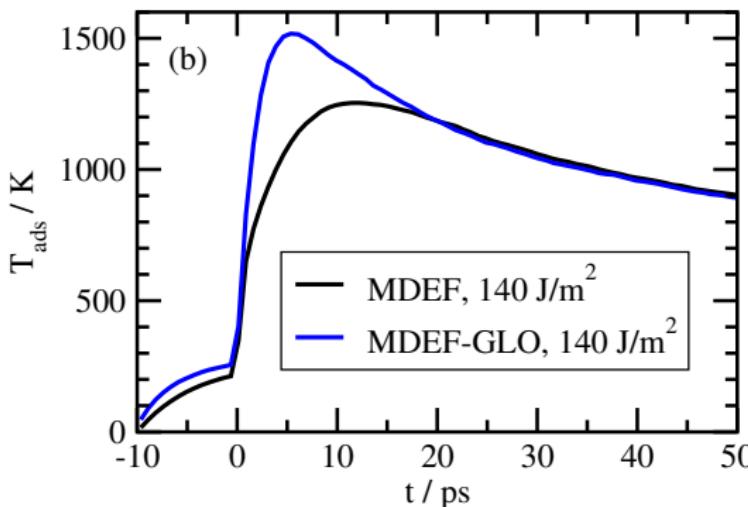
ohne (3): **MDEF**

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

Beispiel CO auf Ru - Diffusion nach Laseranregung



Beispiel CO auf Ru - Adsorbattemperatur



simulierte Adsorbattemperatur T_{ads}

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

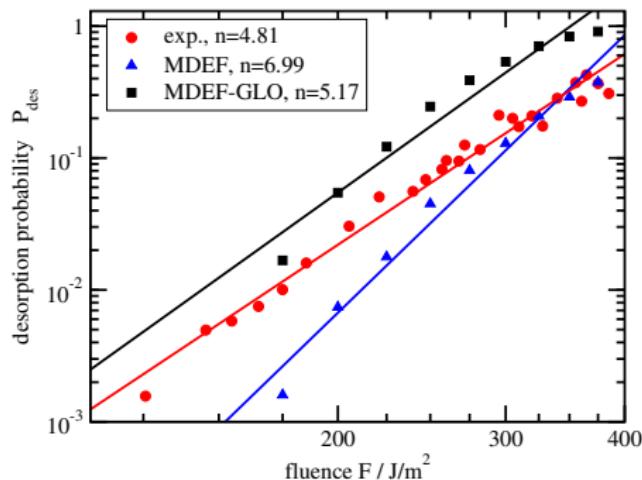
TPD-Spektrum

- Desorption bereits ab 450K erwartet

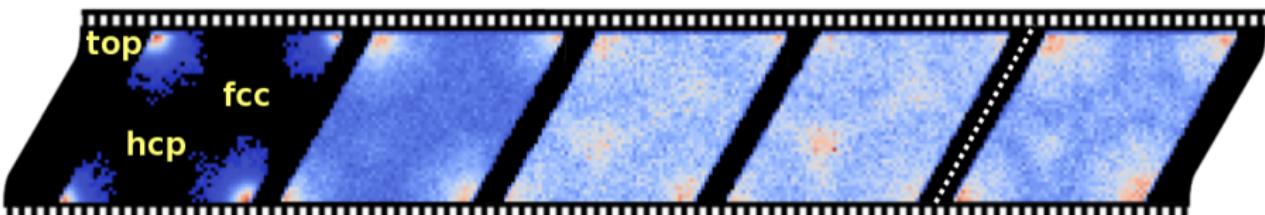
Beispiel CO auf Ru - Lasergetriebene Desorption

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

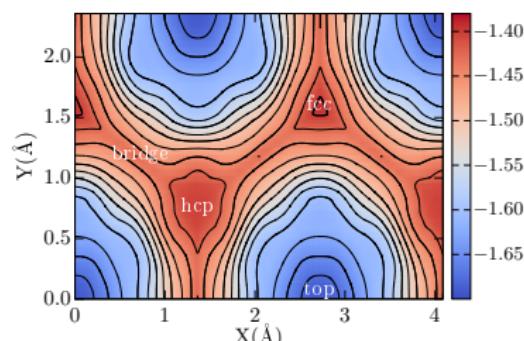


Beispiel CO auf Ru - “dynamischer Fallen-Effekt”



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, H₂/D₂/Ru
- Verbesserungen der Methoden, z.B. Reibung, 2T-Modell
- komplexeres Modell, z.B. mehrere Adsorbatmoleküle

Danksagung

Vielen Dank...

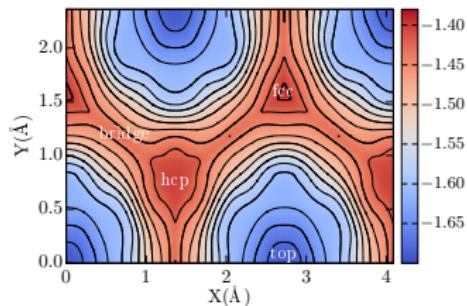
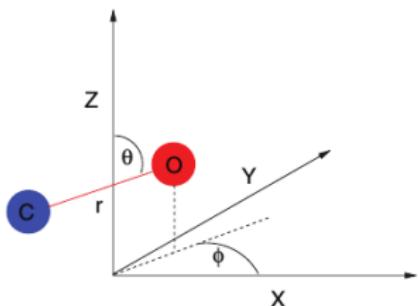
- ... für die wunderbare Betreuung, sowohl fachlich als auch menschlich, an Prof. Peter Saalfrank!
- ... für die tolle Arbeitsatmosphäre an die gesamte Arbeitsgruppe, insbesondere Büro D2.04/05!



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)

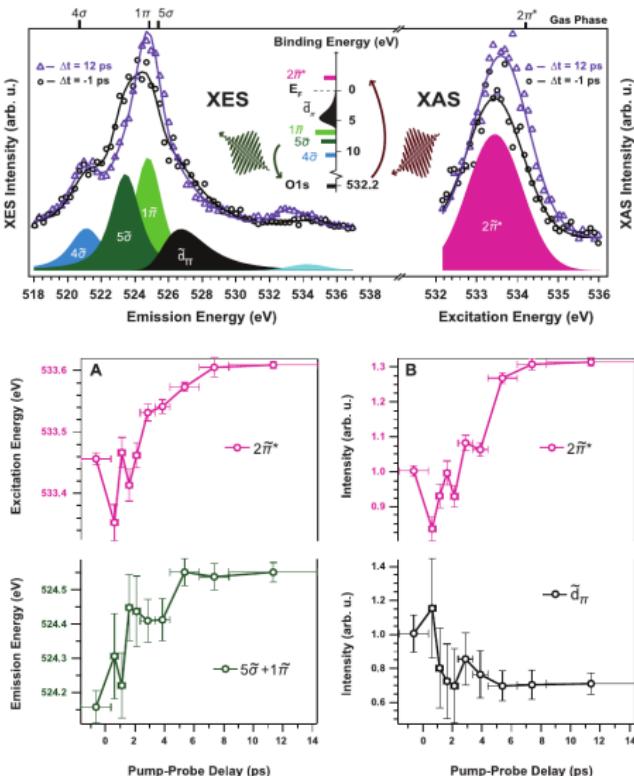
What was done?

- 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}_{π} \Rightarrow decrease by $\sim 30\%$
 - participant peak appears

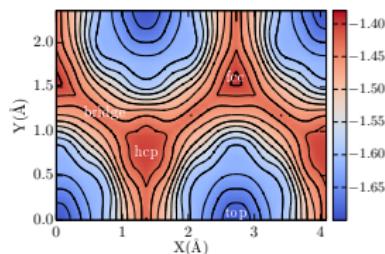
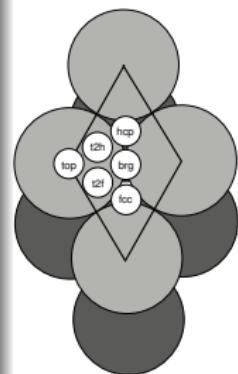
\Rightarrow physisorbed precursor(?)



More facts about the potential energy surface (PES)

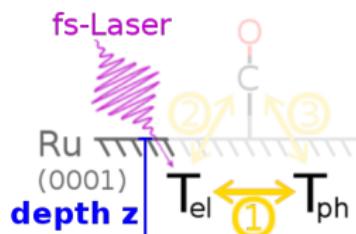
How was it constructed?

- 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

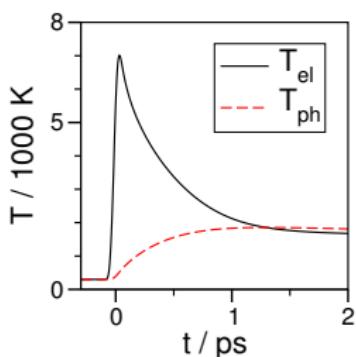


Two-temperature model (TTM)

Two coupled heat diffusion equations



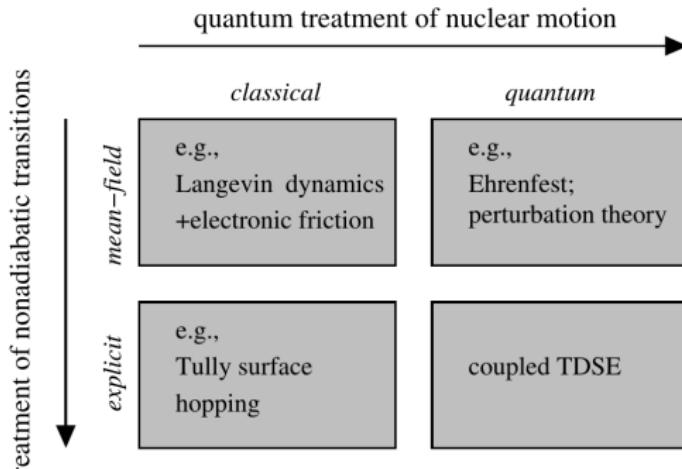
$$\begin{aligned} & \text{Heat diffusion along z-direction} \\ C_{\text{el}} \frac{\partial T_{\text{el}}}{\partial t} = & \underbrace{\frac{\partial}{\partial z} \kappa \frac{\partial}{\partial z} T_{\text{el}}}_{\text{Heating/cooling rate at depth } z} - g(T_{\text{el}} - T_{\text{ph}}) + S(z, t),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



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

- T_{el} and T_{ph} as $f(z, t)$ from laser/material properties
 - C_{el} and C_{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, λ , fluence F

Different approaches to non-adiabatic coupling

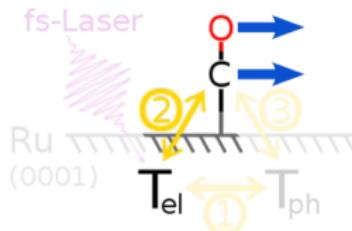


Langevin dynamics + electronic friction

- 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.)

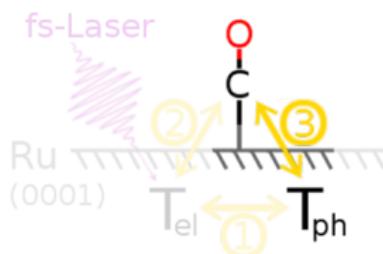
- friction coefficient of Atom k : $\eta_{el,k}(\underline{r}_k) \Rightarrow$ dissipation
 - derived from local density friction approximation (LDFA)
⇒ individual atom (again IAA) in free electron gas
 - $\eta_{el,k}(\underline{r}_k)$ dependent on electron density of bare surface
- random force $R_{el,k}(t) \Rightarrow$ 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

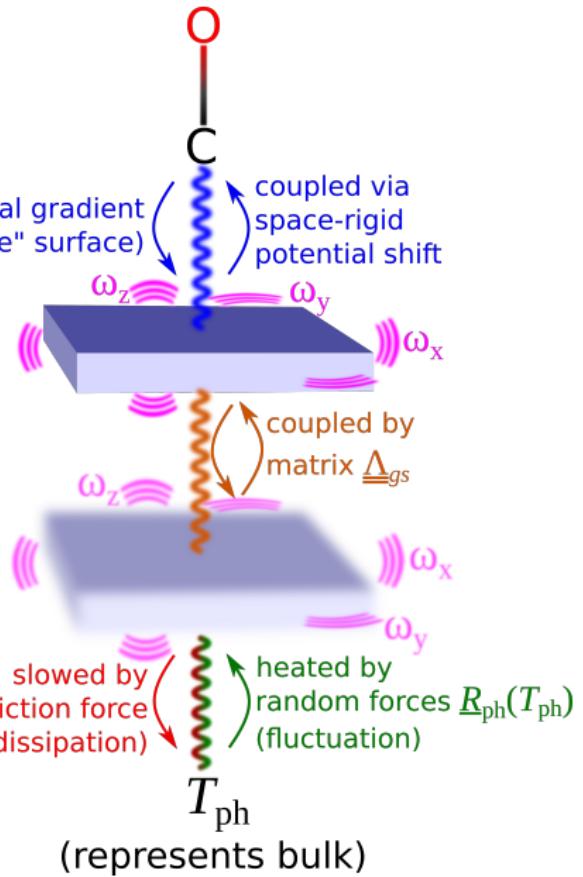
both oscillate in the
3 dimensions x, y, z

Ghost oscillator

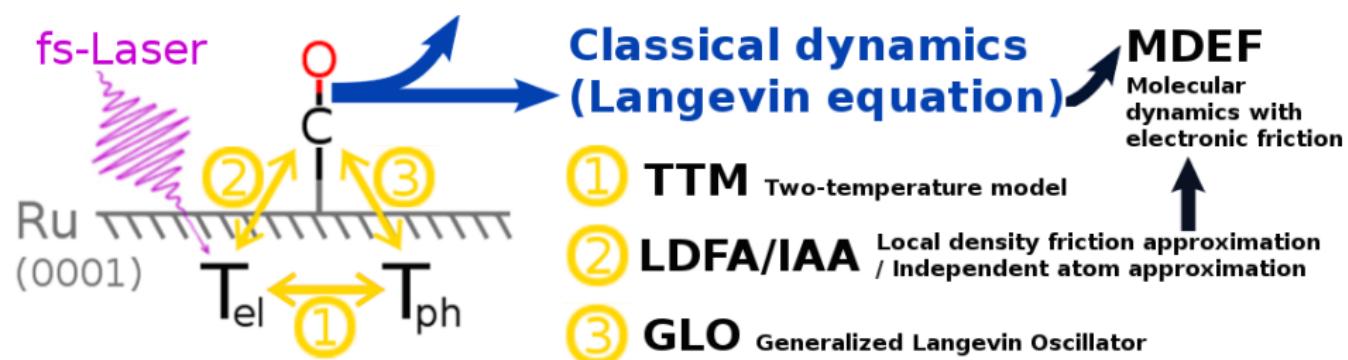
\underline{r}_g

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

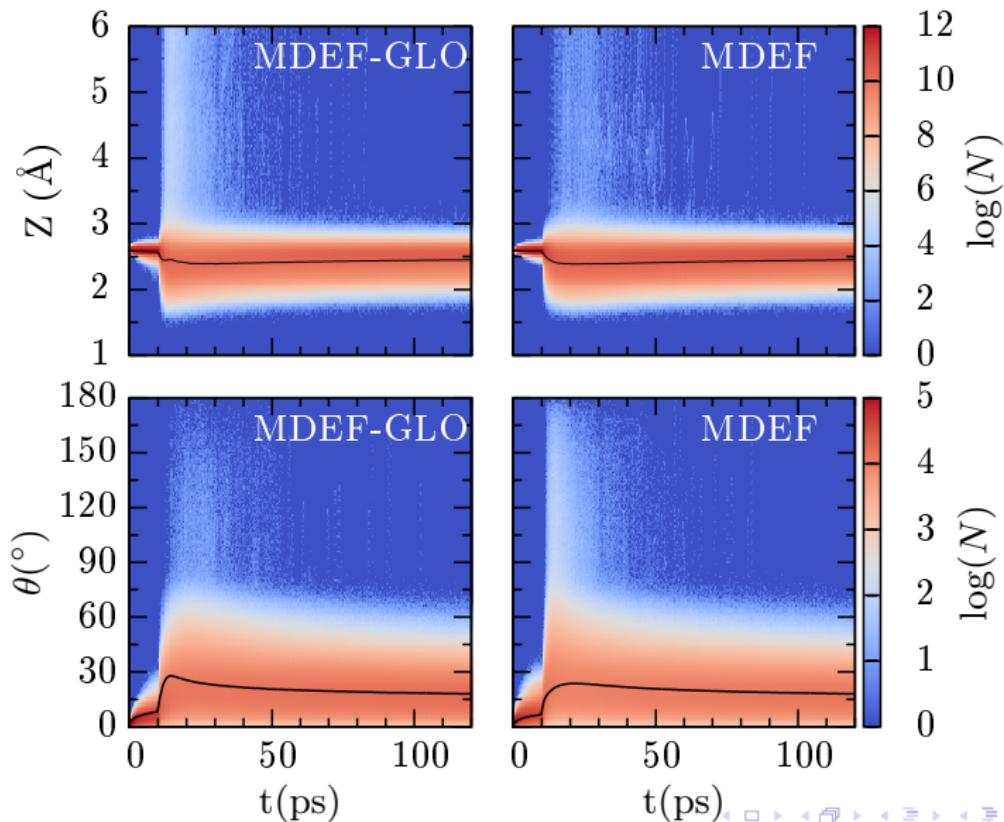
Harmonic oscillator Coupling to surface oscillator Friction force Random forces



Summary of models and methods

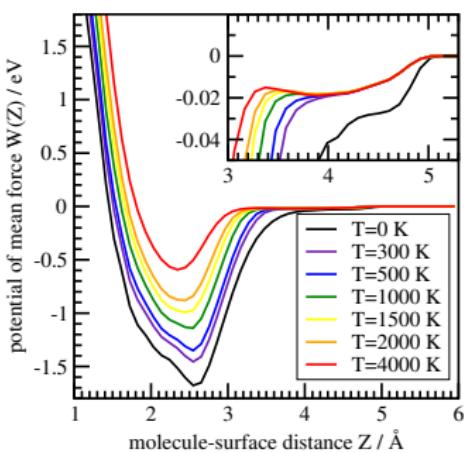
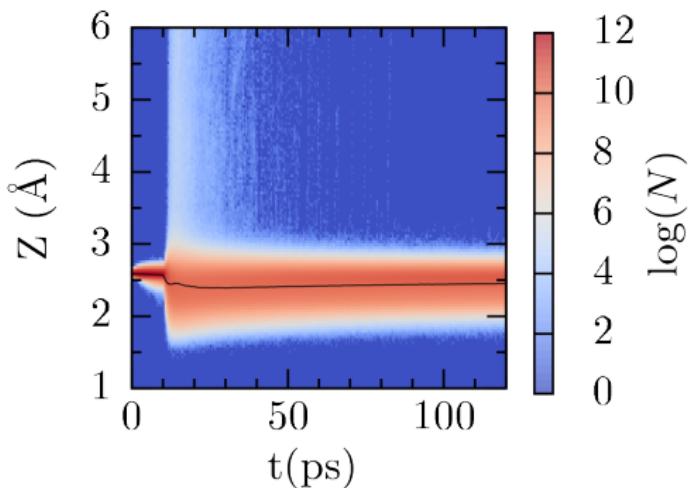


Heating of DOFs Z and θ



No population of physisorbed state in our dynamics

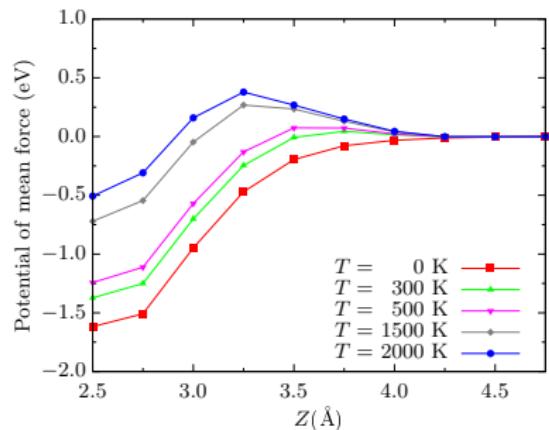
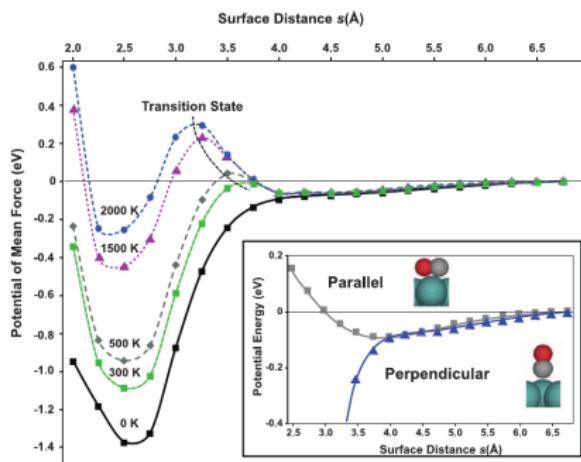
As is to be expected from negligible barrier in potential of mean force (PMF)



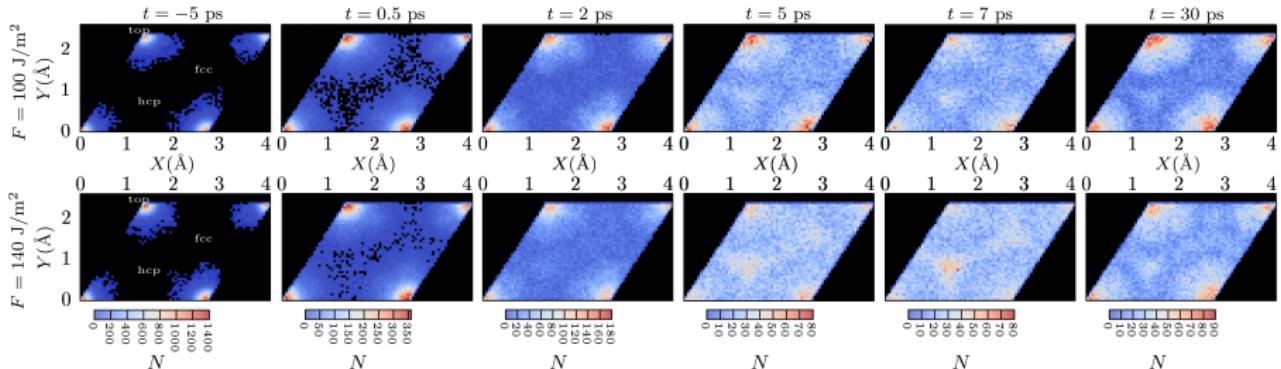
Why are the entropic barriers of the PMFs so different?

Because separability assumption fails clearly

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

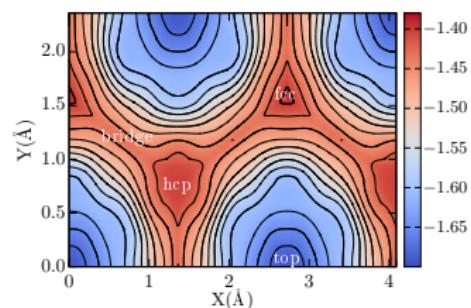


Dynamical trapping: alternative/additional explanation?

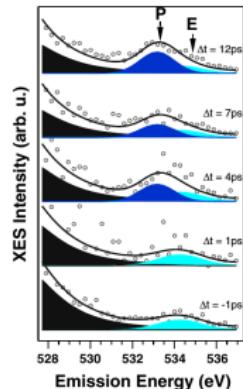
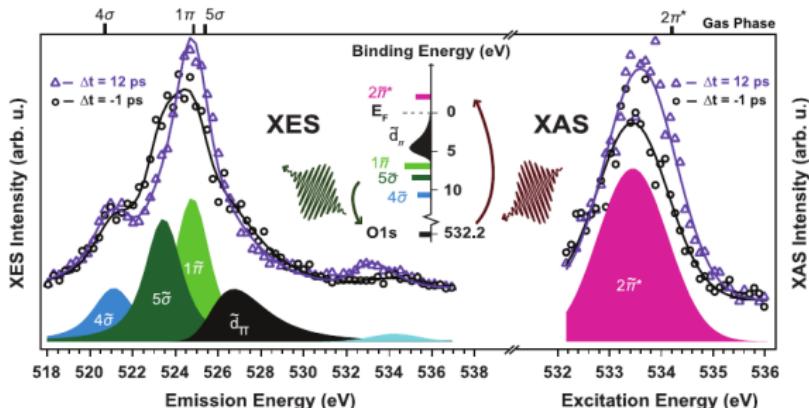


Surprising patterns in XY-distribution

- 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?



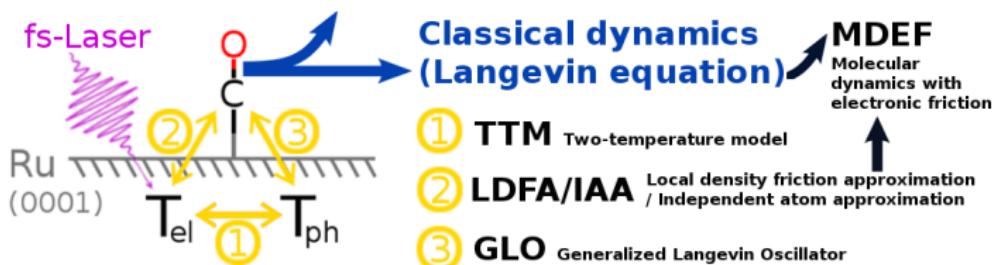
Dynamical trapping can't explain all observations

- 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), H₂/Au(111) etc.