

Laser-driven dynamics of CO on Ru(0001)

A computational study using electronic friction (MDEF) and the generalized Langevin oscillator (GLO)

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Outline

1 Introduction

- Motivation - in general and system specific
- First impressions of fs-laser-driven dynamics

2 Models and methods

- Foundations: 6D potential and two-temperature model
- Electronic friction: non-adiabatic coupling approximated
- The generalized Langevin oscillator (GLO)
- “Half-time”: short summary (and maybe time for a few questions)

3 Results and discussion

- Laser-driven diffusion and desorption
- Physisorbed precursor states?

4 Summary and Outlook

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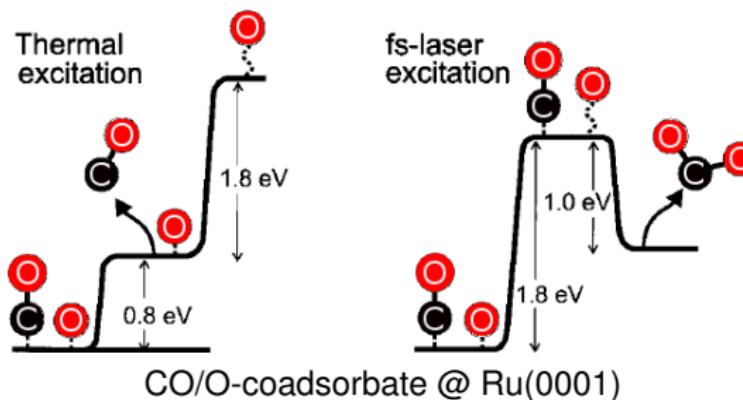
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General motivation

Why investigate fs-laser-driven surface dynamics?

- gain fundamental understanding of adsorbate bonding
⇒ additional tool besides scattering experiments and STM
- possible direct application in catalysis: “femtochemistry”
⇒ new reaction pathways opened up by fs-lasers



M. Bonn *et al.*, *Science* 1999

Specific motivation for investigating CO/Ru(0001)

CO/Ru(0001) system important for catalysis, e.g.:

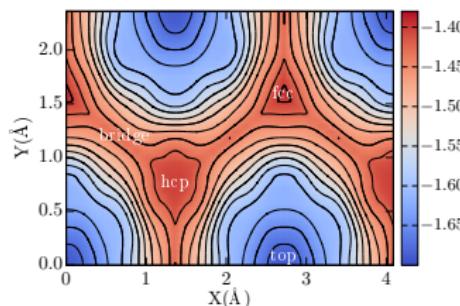
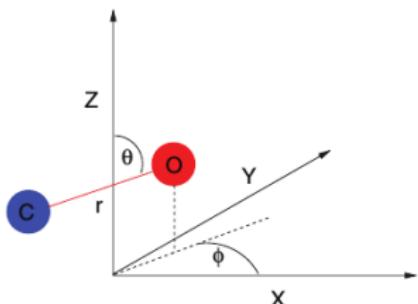
- Fischer-Tropsch synthesis ($n\text{CO} + 2n\text{H}_2 \rightarrow$
Alkane/Alkene/Alkohole + H_2O)
- exhaust gas converters (cars, power plants, etc.)

Experimentally well studied system

- especially regarding fs-laser irradiation:
 - e.g. Bonn *et al.*, *Science* 1999; Funk *et al.*, *JChemPhys* 2000
 - (both Ertl group ⇒ chemistry Nobel prize 2007).
- desorption kinetics: large prefactors ⇒ still not understood
- recently, time resolved x-ray spectra (XAS and XES)
⇒ “movie” of changes in orbital density of states
 - Dell'Angela *et al.*, *Science* 2013

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!**

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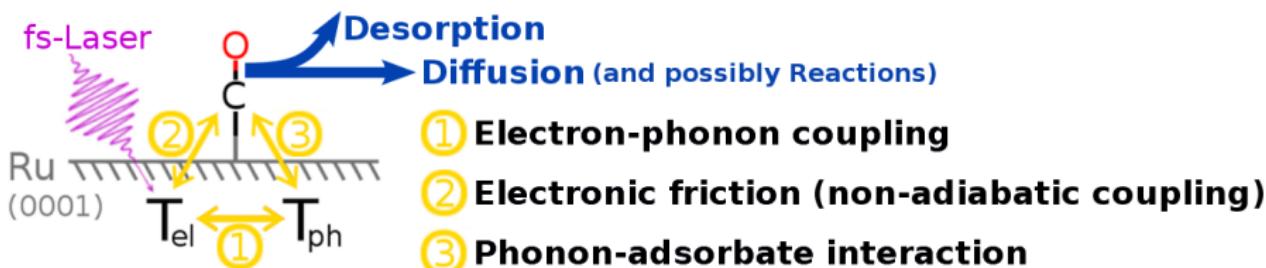
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4

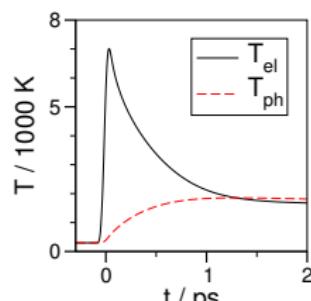
Summary and Outlook

What happens after fs-laser excitation of the metal?



Coupling between 3 kinds of degrees of freedom:

- electron gas (T_{el})
 - initially absorbs laser energy
 - low heat capacity \Rightarrow high T_{el} ($\approx 5\text{-}10 \text{ kK}$)
- lattice vibrations (T_{ph})
 - thermalization with electrons: ps time scale
 \Rightarrow fs-laser causes two distinct temperatures!
- adsorbate movement (T_{ads})



Details of the time-resolved x-ray experiment

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

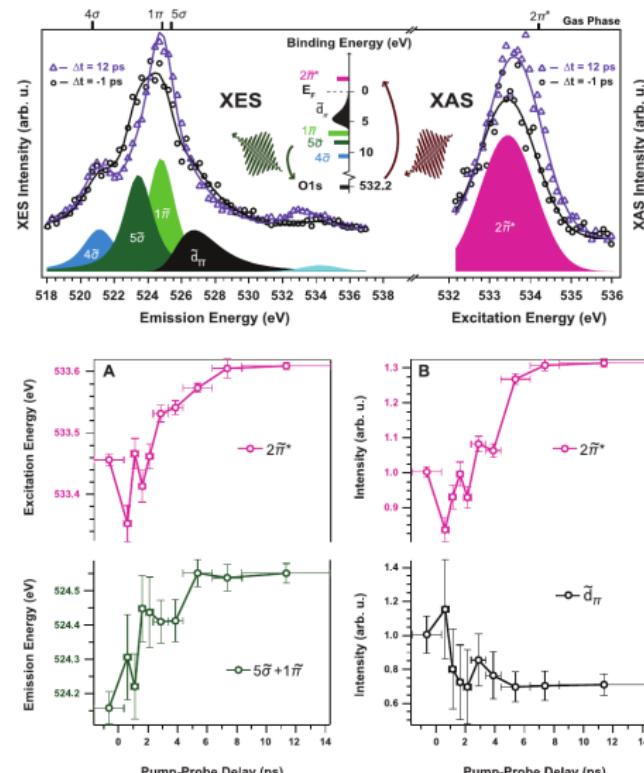
What was done?

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

What is observed?

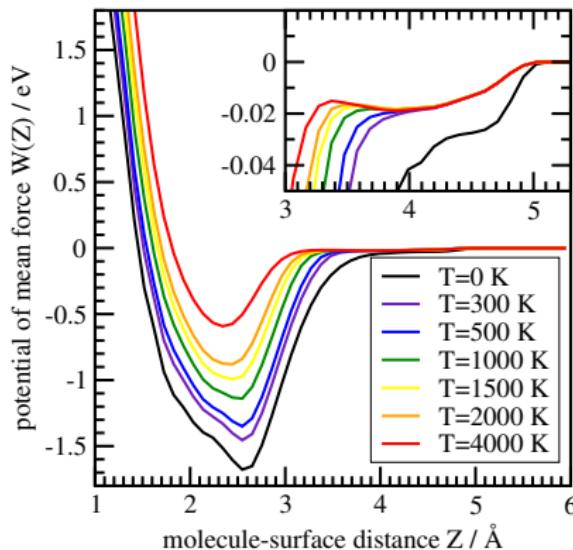
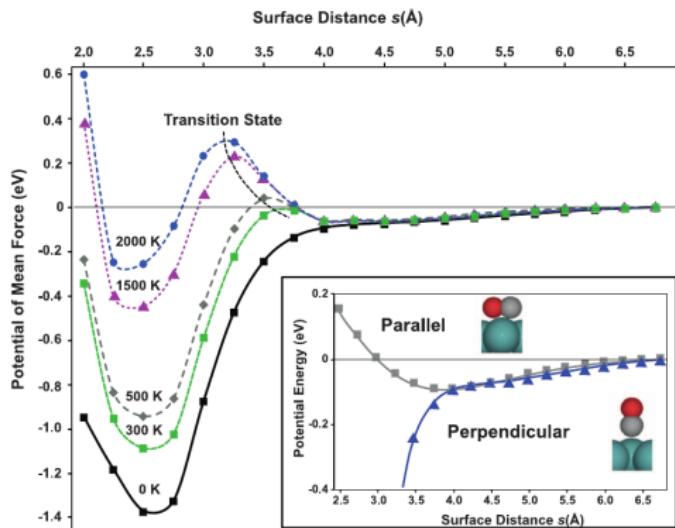
- orbital density of states at O
- energies shift towards gas-phase values of CO
- intensities change
 - $2\tilde{\pi}^*$ \Rightarrow increase by $\sim 30\%$
 - \tilde{d}_π \Rightarrow decrease by $\sim 30\%$
 - participant peak appears

\Rightarrow physisorbed precursor(?)



Details of the accompanying theory

still Dell'Angela *et al.*, *Science* 2013 (theory part by Nørskov group, SUNCAT, Stanford)



Dell'Angela *et al.*, *Science* 2013

Scholz *et al.*, *PhysRevB* 2016

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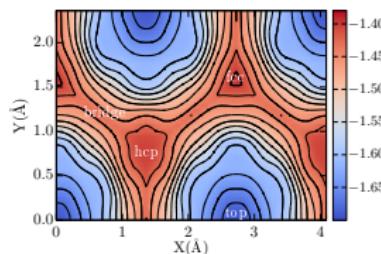
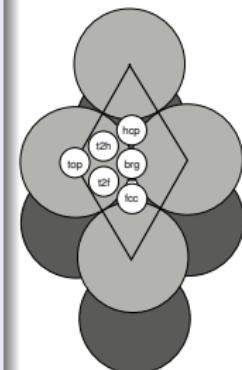
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More facts about the potential energy surface (PES)

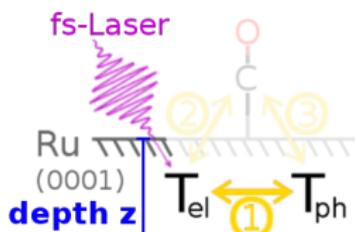
How was it constructed?

- 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

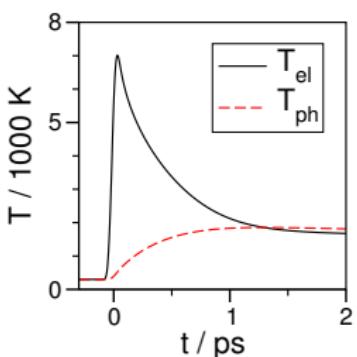


Two-temperature model (TTM)

Two coupled heat diffusion equations



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



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

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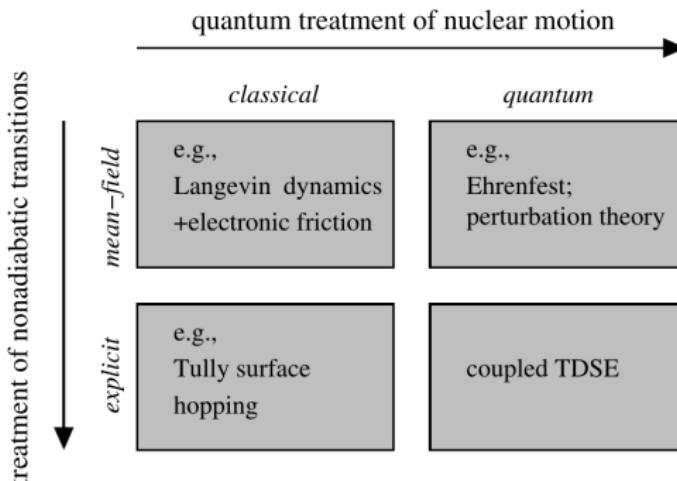
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Different approaches to non-adiabatic coupling

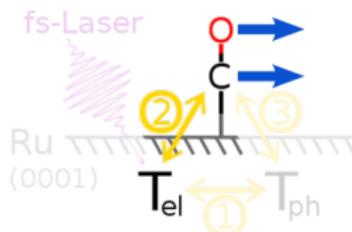


Langevin dynamics + electronic friction

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

The Langevin equation

A stochastic differential equation



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

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)
 \Rightarrow 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 $T_{el}(t)$

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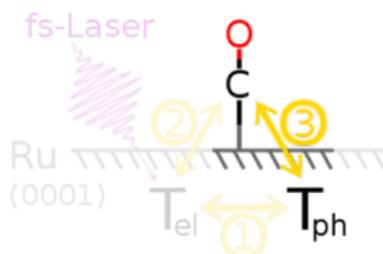
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Generalized Langevin Oscillator

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

Harmonic oscillator Coupling to ghost oscillator

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



Surface oscillator
 \underline{r}_s

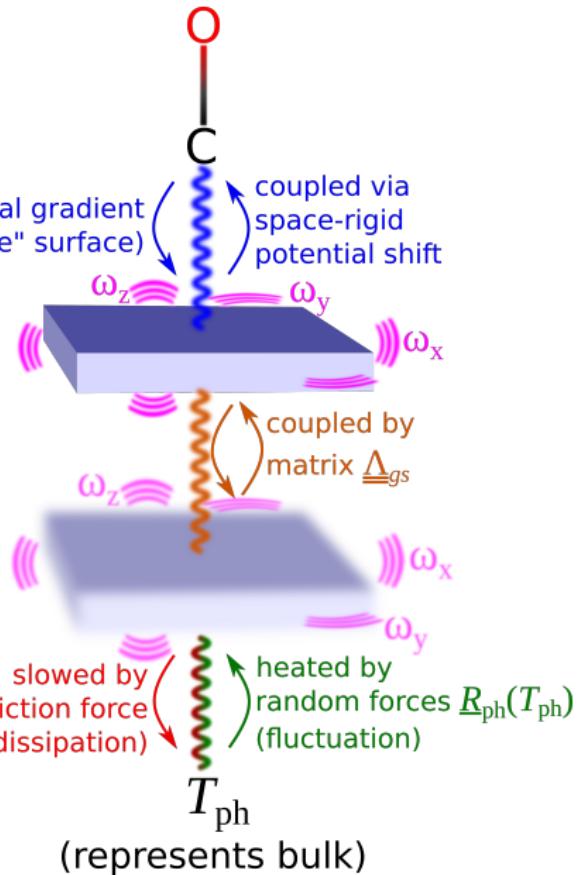
both oscillate in the
3 dimensions x, y, z

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



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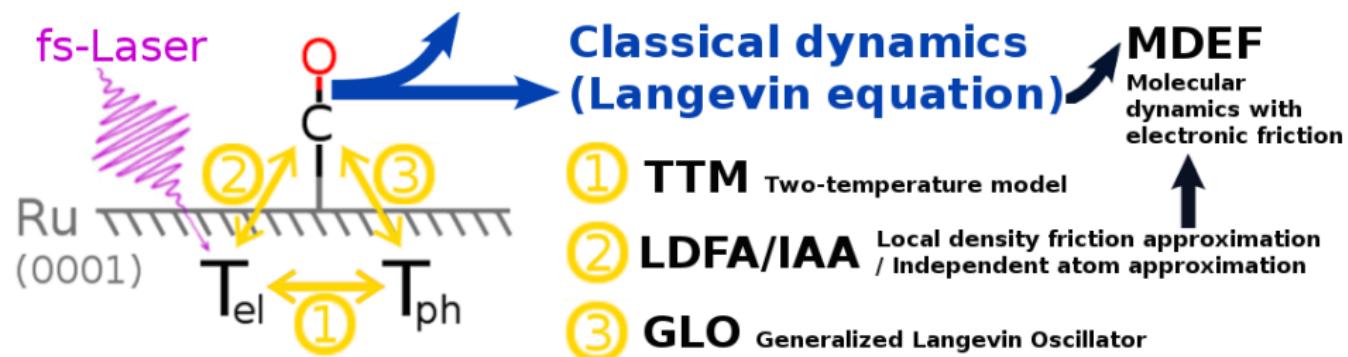
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Summary of models and methods



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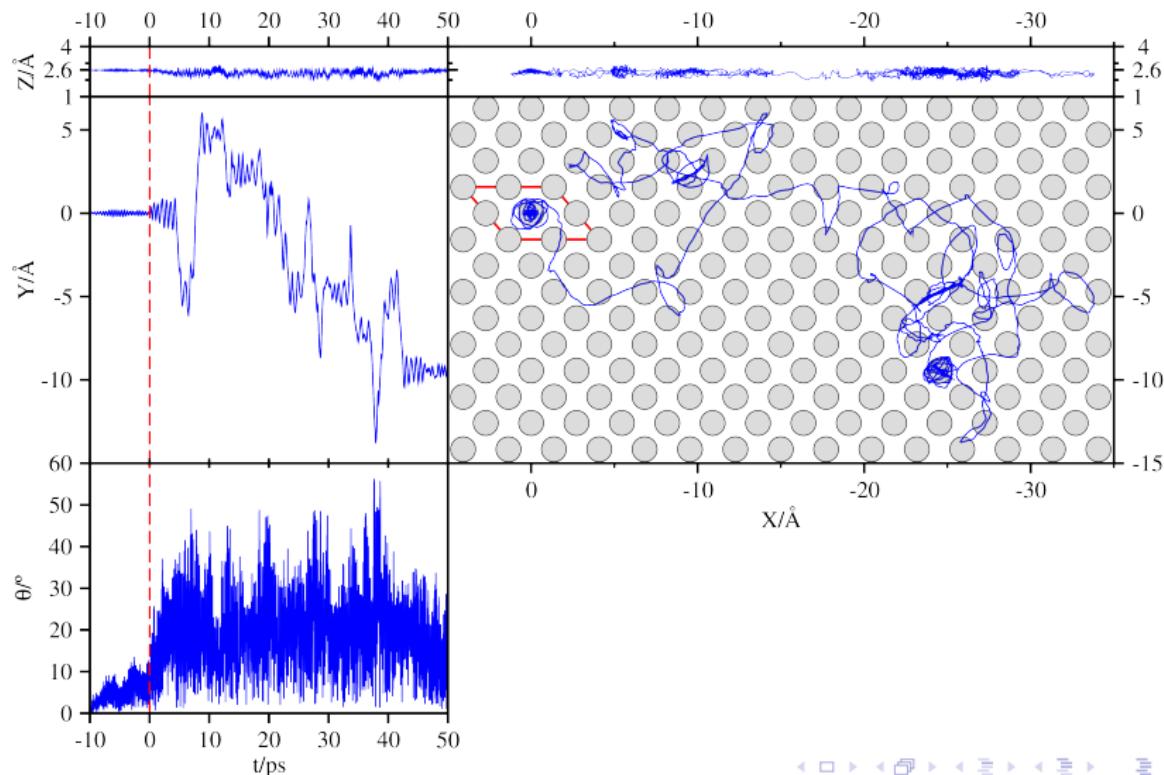
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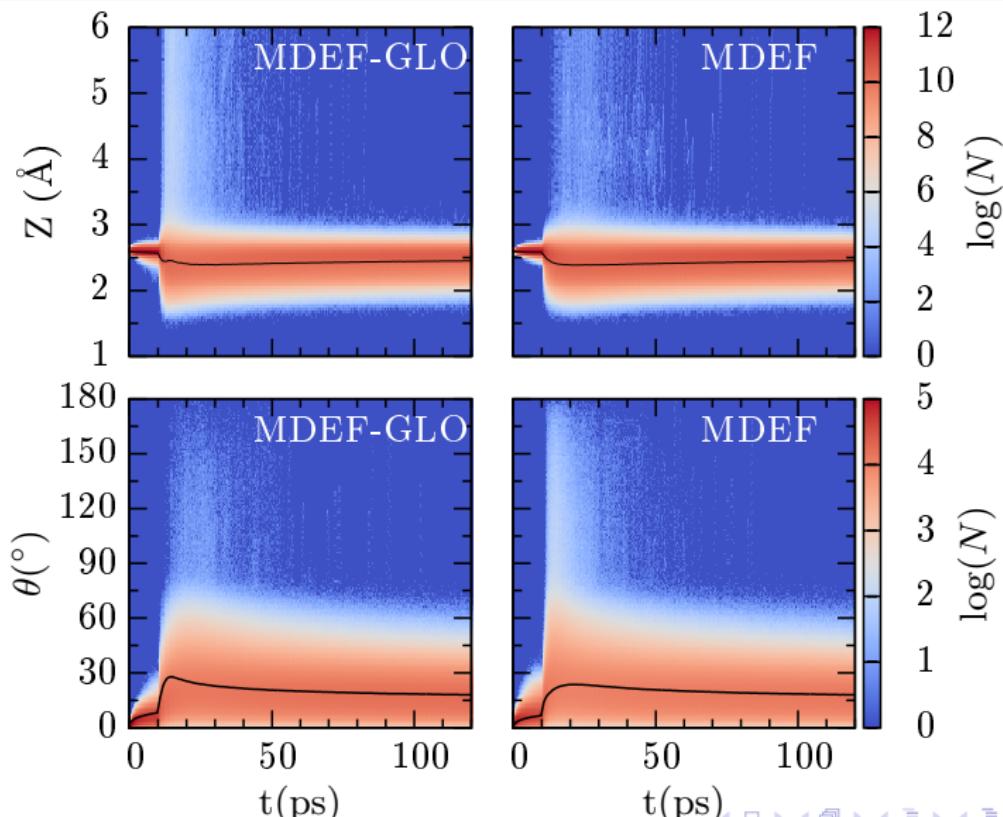
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Example trajectory

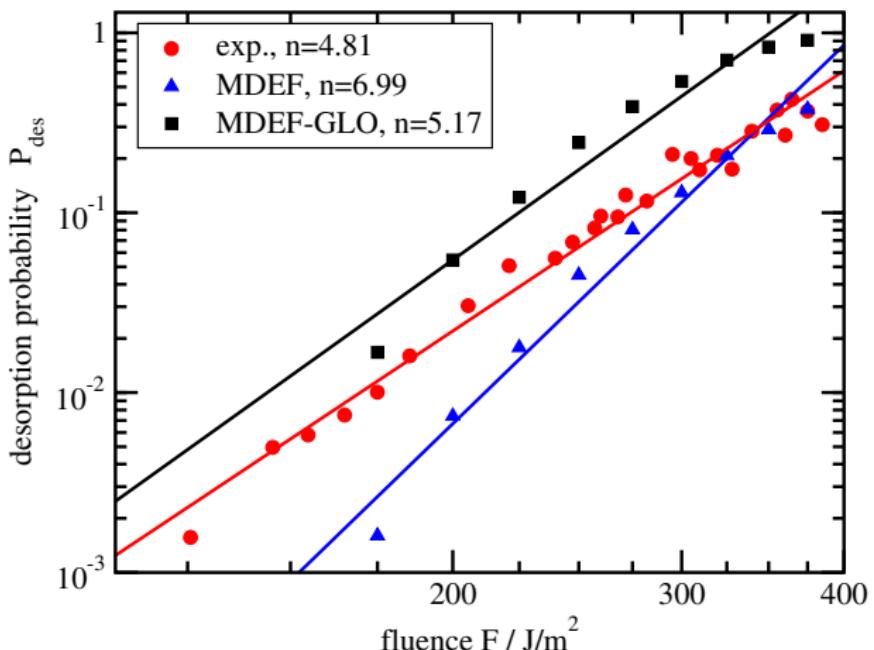
(in this case without GLO-model)



Heating of DOFs Z and θ



Fluence-dependence of desorption yield P_{des}



Power-law

- $P_{\text{des}} = A \cdot F^n$
- not exactly

Differences in exp.

- coverage:
⇒ 0.68 ML (max.)

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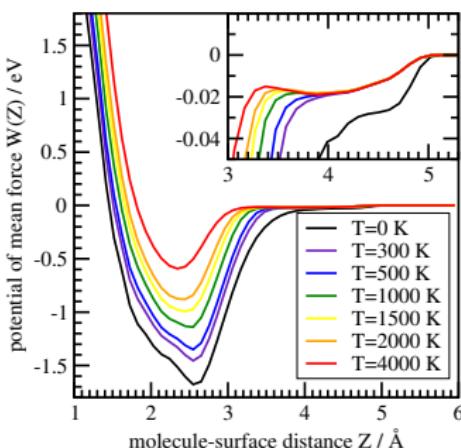
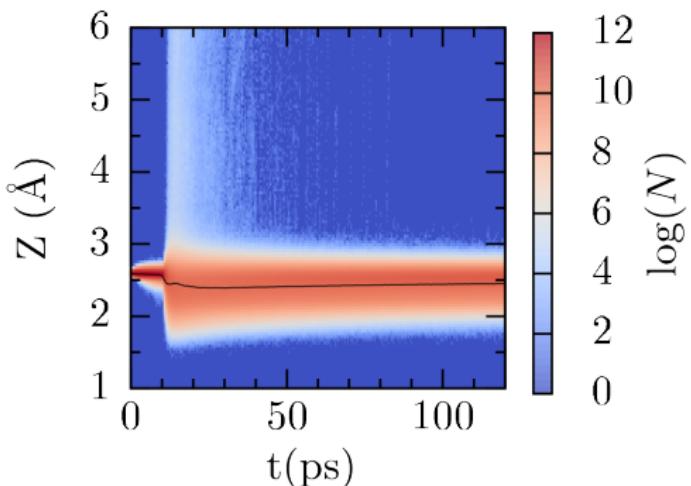
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No population of physisorbed state in our dynamics

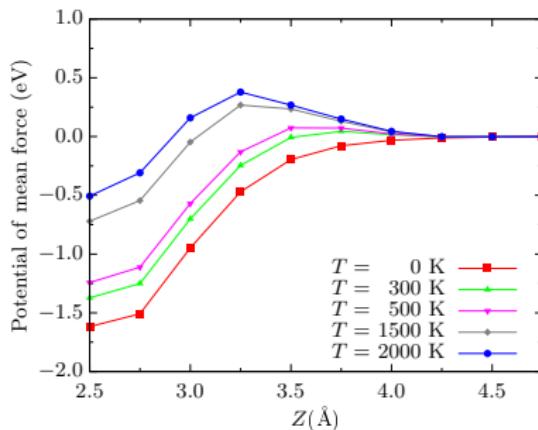
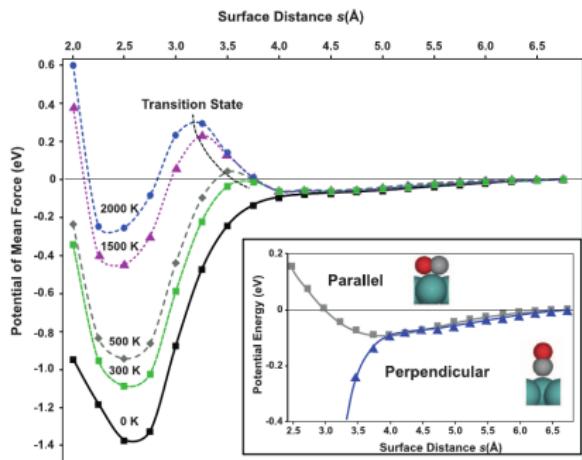
As is to be expected from negligible barrier in potential of mean force (PMF)



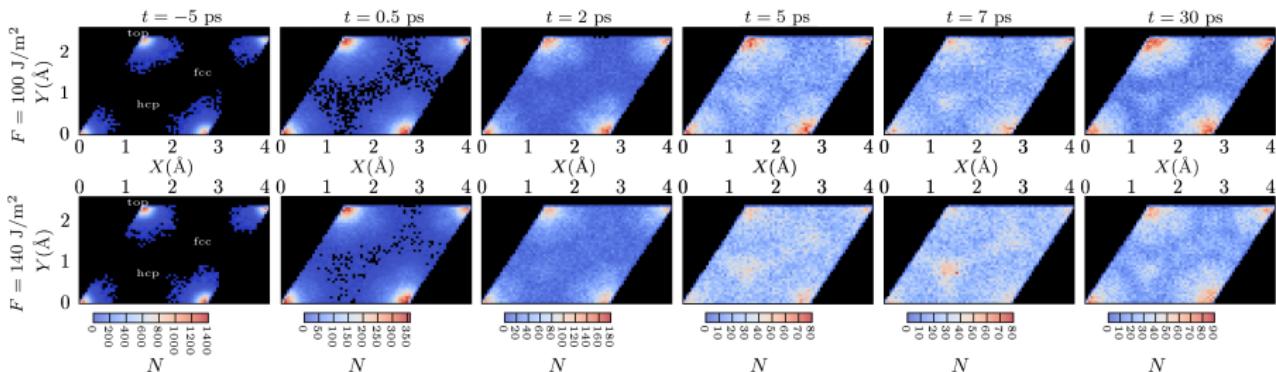
Why are the entropic barriers of the PMFs so different?

Because separability assumption fails clearly

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

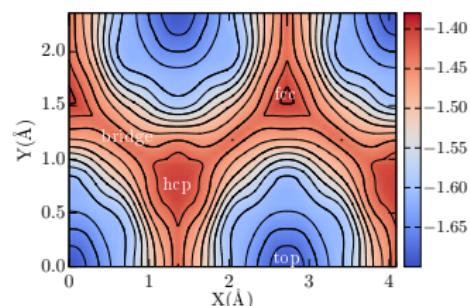


Dynamical trapping: alternative/additional explanation?

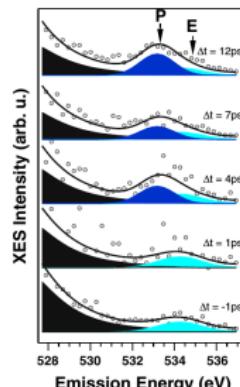
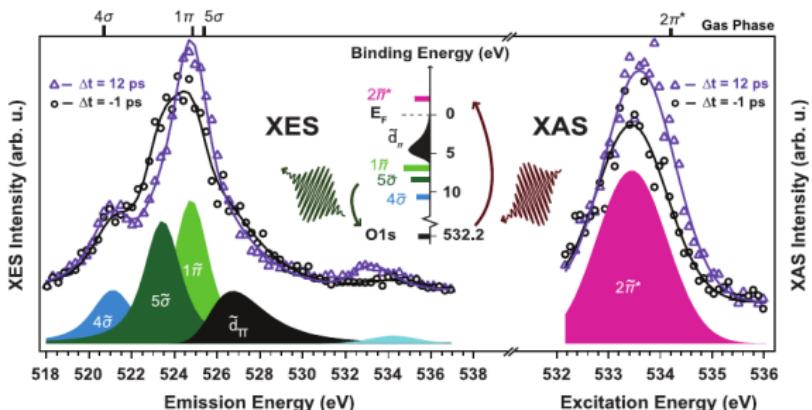


Surprising patterns in XY-distribution

- 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: $2\tilde{\pi}^*$ -intensity not increased (computed by Christopher)
- participant 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

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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.

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- Peter, for all his support and particularly for writing the paper
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