

# 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

- Overview of computational settings
- Laser-driven diffusion and desorption
- Physisorbed precursor states?

## 4 Summary and Outlook

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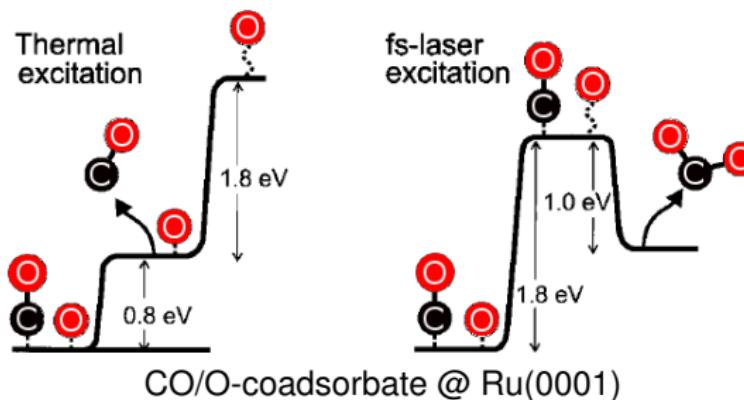
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# General motivation

## 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.:

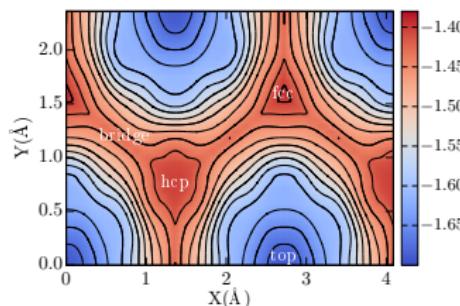
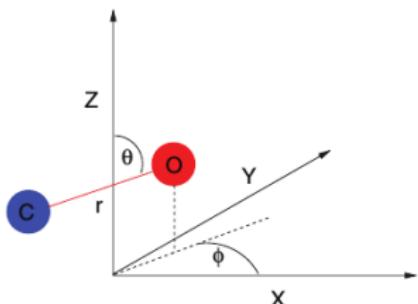
- Fischer-Tropsch synthesis ( $n\text{CO} + 2n\text{H}_2 \rightarrow$   
Alkane/Alkene/Alkohole +  $\text{H}_2\text{O}$ )
- exhaust gas converters (cars, power plants, etc.)

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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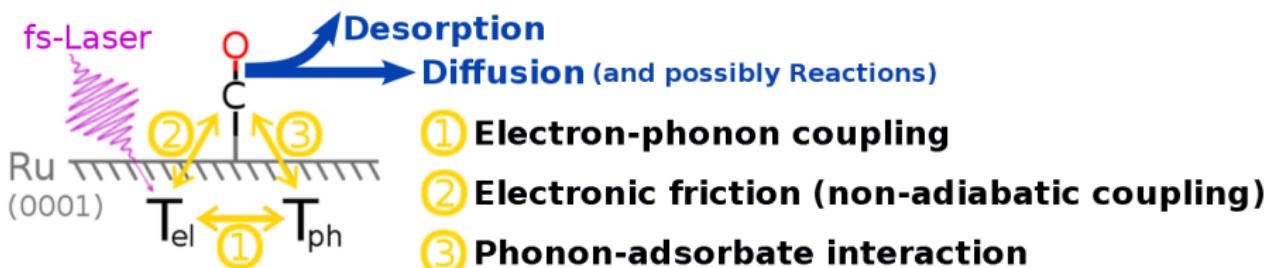
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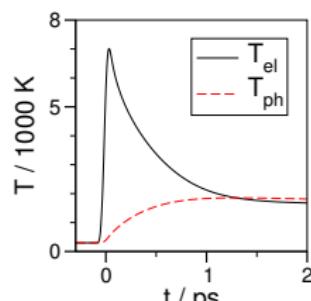
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# What happens after fs-laser excitation of the metal?



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)

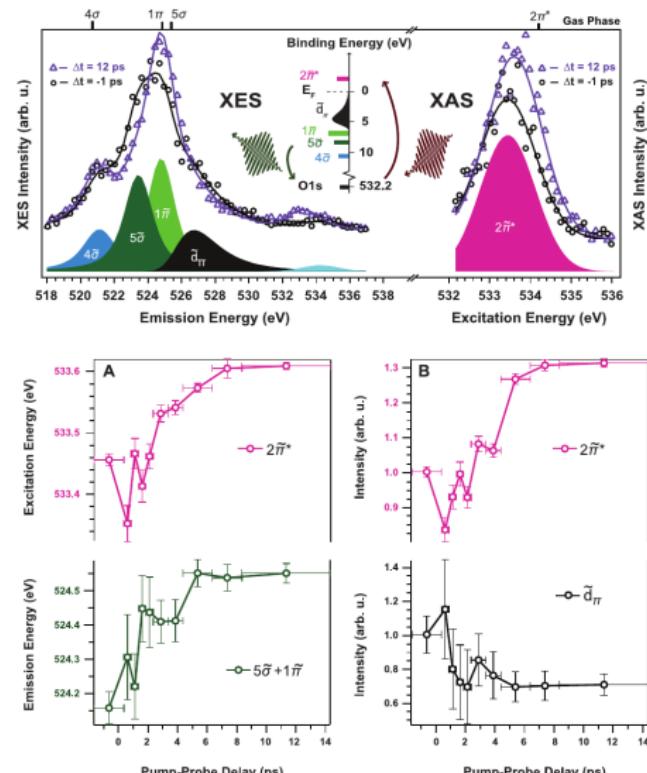
## What was done?

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

## What is observed?

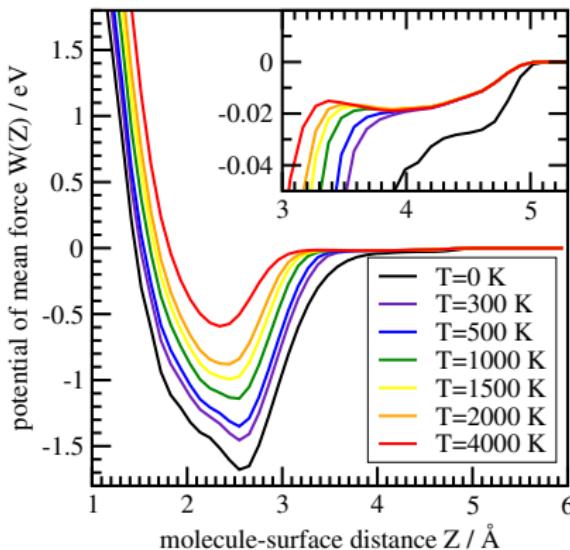
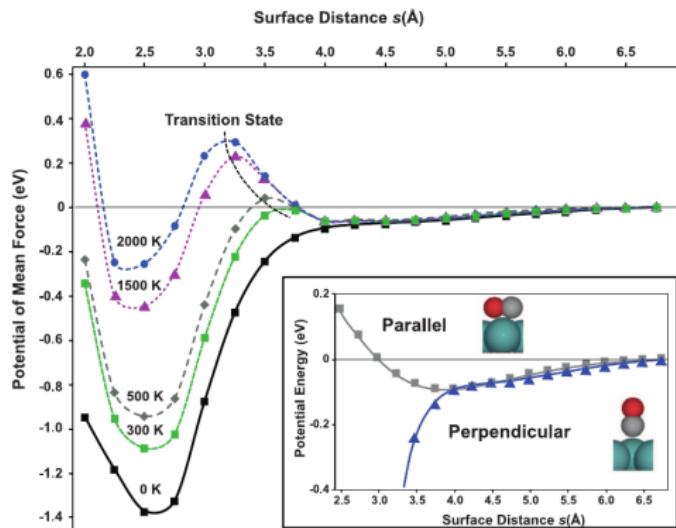
- orbital density of states at O
- energies shift towards gas-phase values of CO
- intensities change
  - $2\tilde{\pi}^*$   $\Rightarrow$  increase by  $\sim 30\%$
  - $\tilde{d}_\pi$   $\Rightarrow$  decrease by  $\sim 30\%$
  - participant peak appears

$\Rightarrow$  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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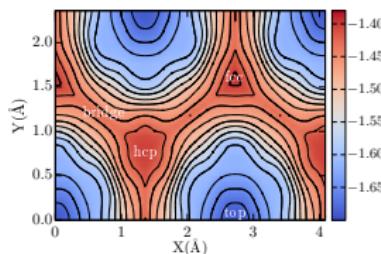
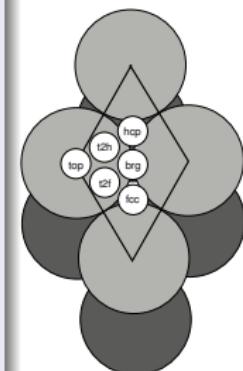
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# More facts about the potential energy surface (PES)

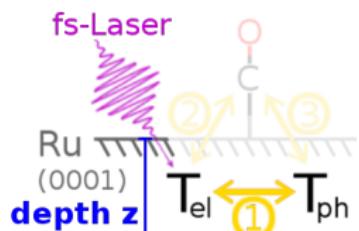
## How was it constructed?

- 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

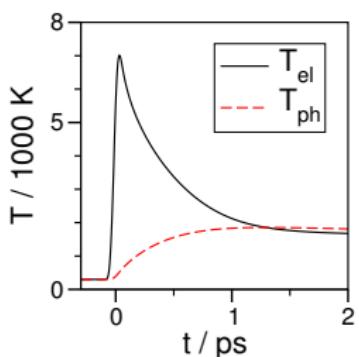


# Two-temperature model (TTM)

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)

- $T_{\text{el}}$  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  $F$

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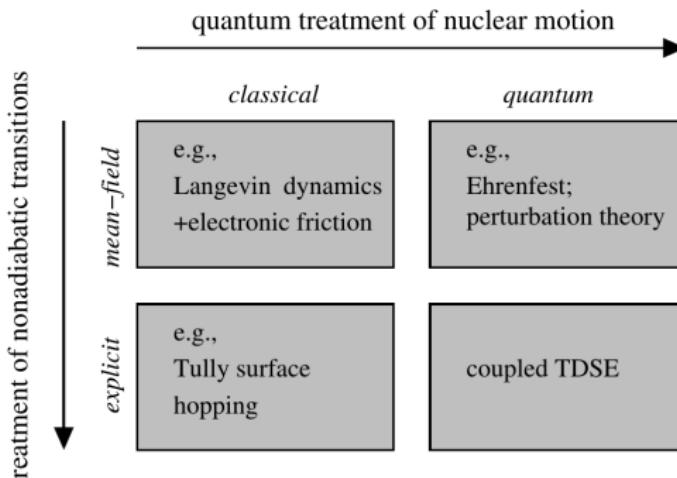
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# Different approaches to non-adiabatic coupling

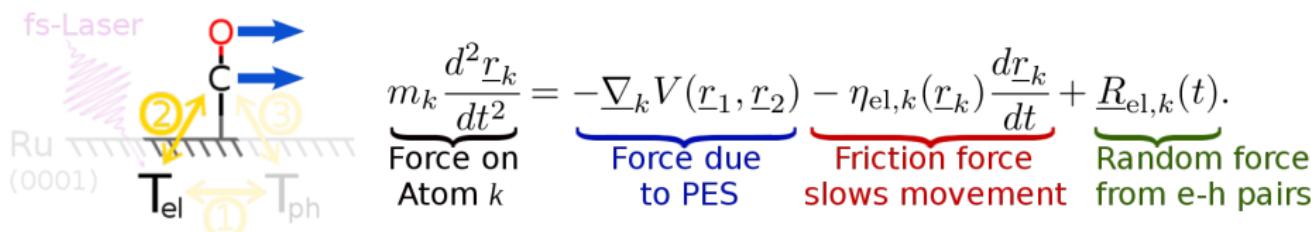


## Langevin dynamics + electronic friction

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

# The Langevin equation

## A stochastic differential equation



### 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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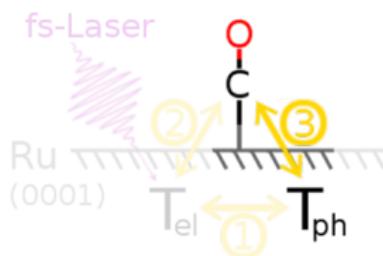
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# Generalized Langevin Oscillator

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

Harmonic oscillator      Coupling to ghost oscillator

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



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

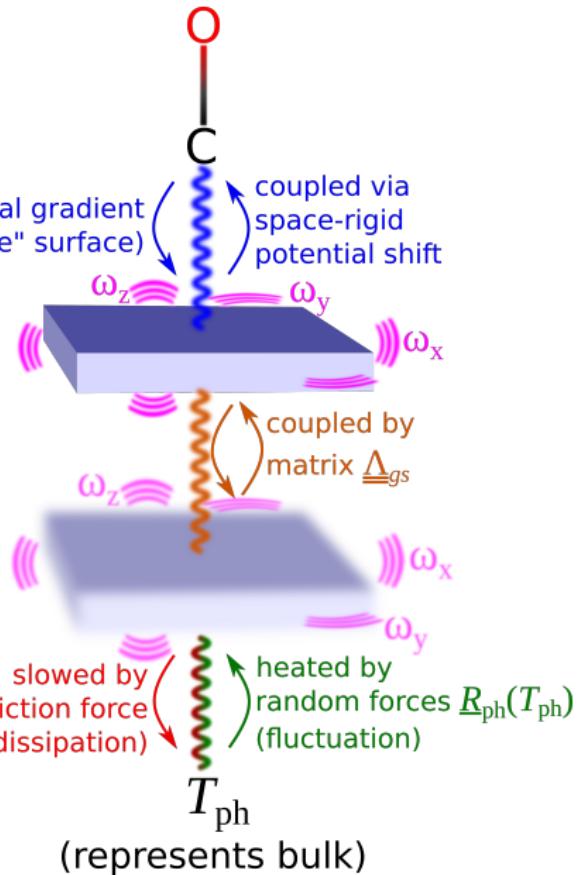
both oscillate in the 3 dimensions x, y, z

**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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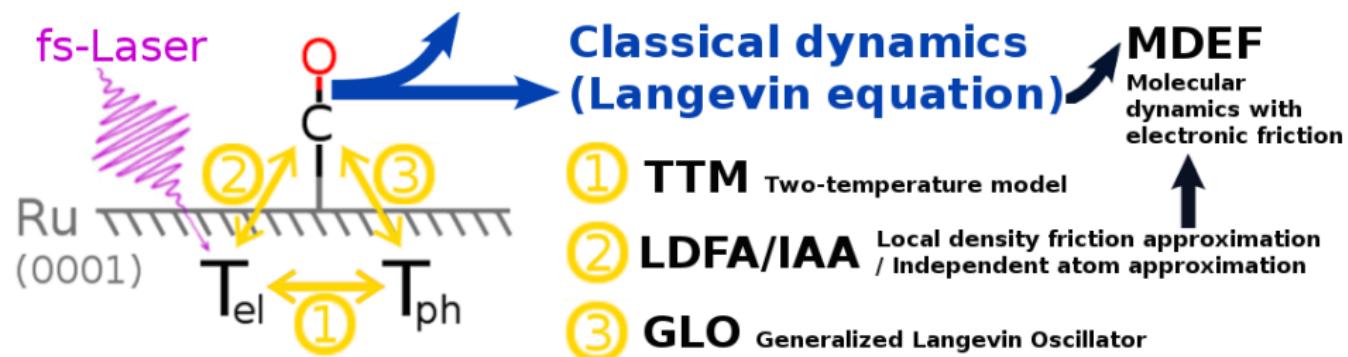
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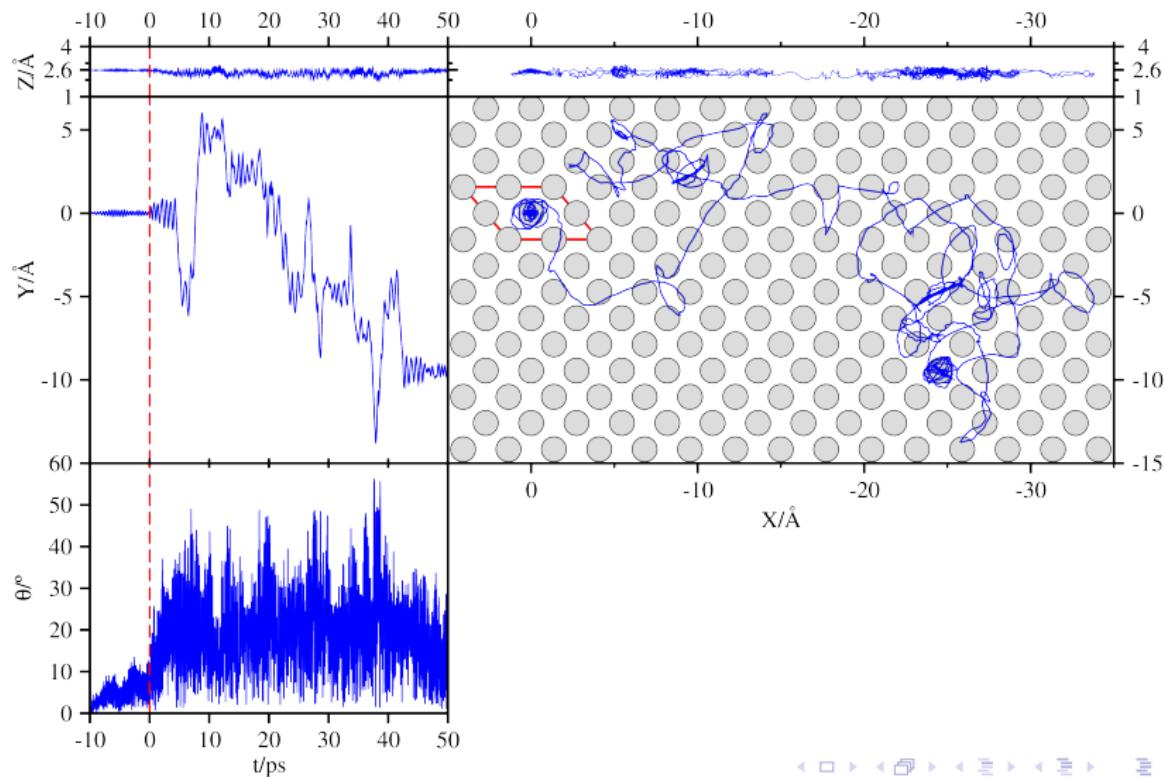
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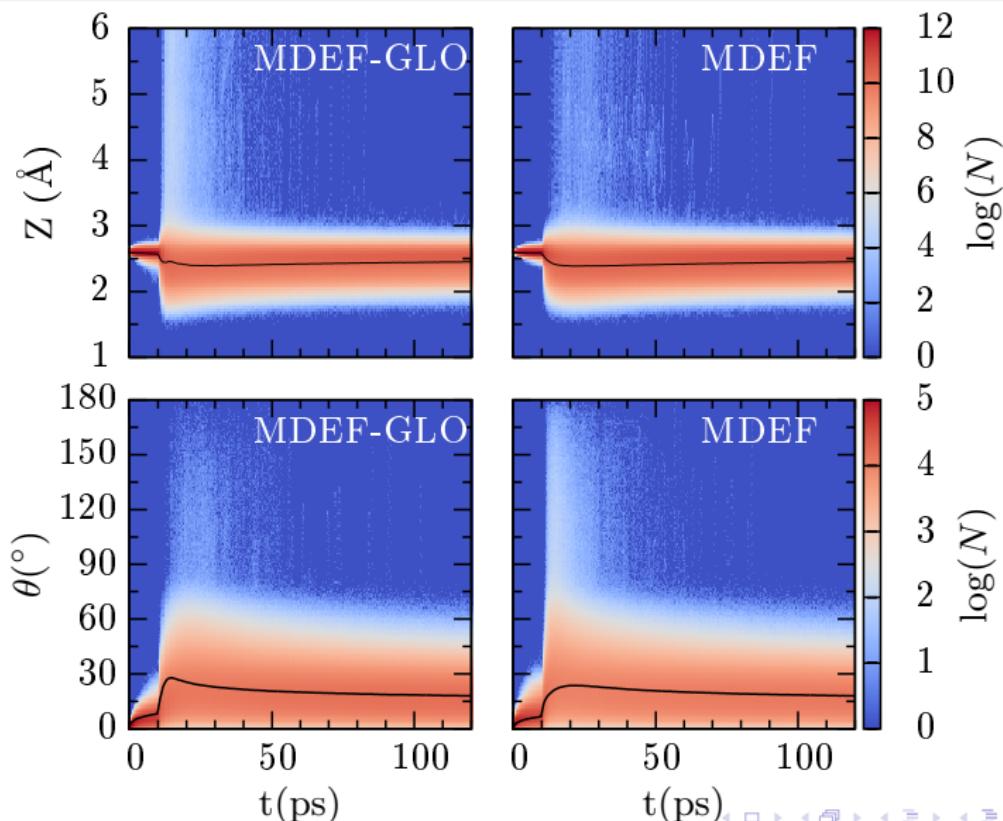
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# Example trajectory

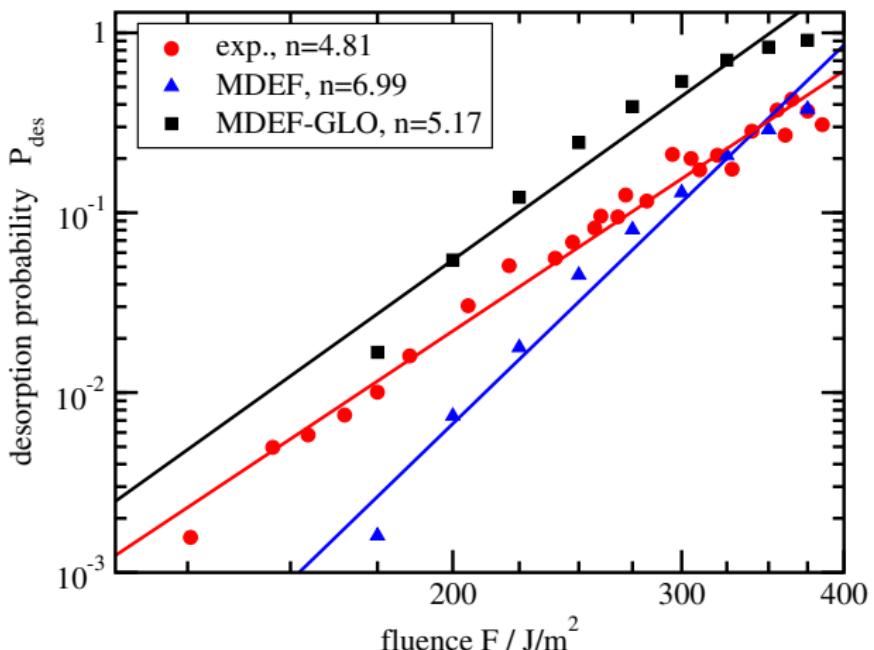
(in this case without GLO-model)



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



# Fluence-dependence of desorption yield $P_{\text{des}}$



## Power-law

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

## Differences in exp.

- coverage:  
⇒ 0.68 ML (max.)

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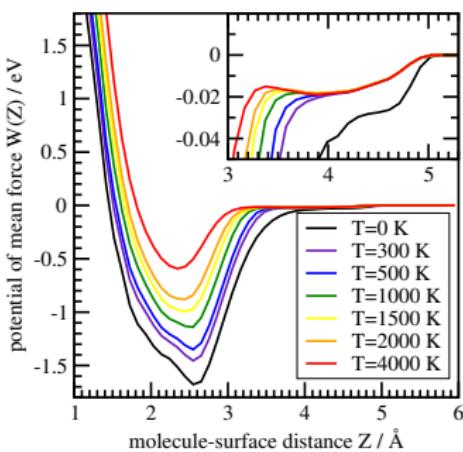
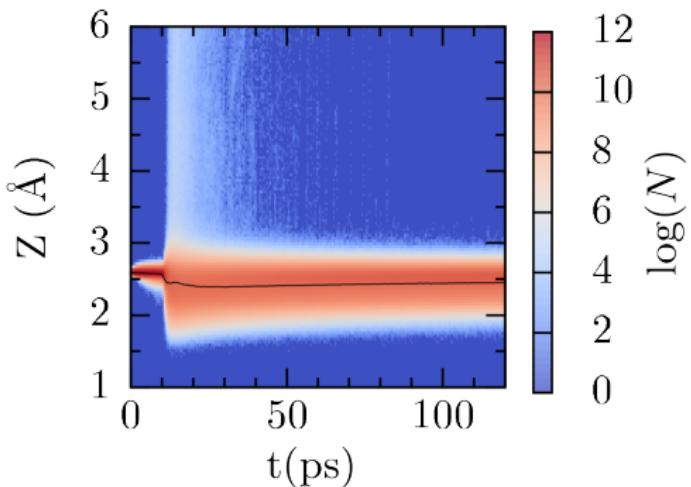
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# No population of physisorbed state in our dynamics

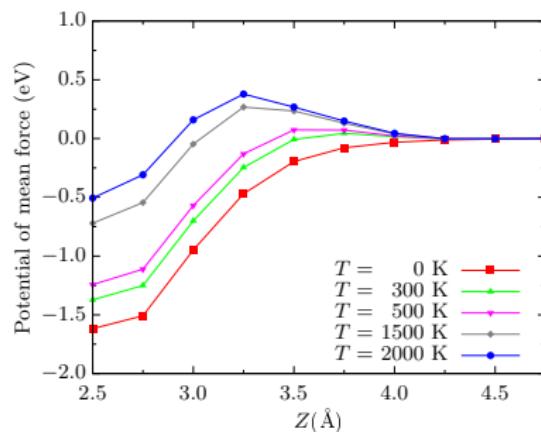
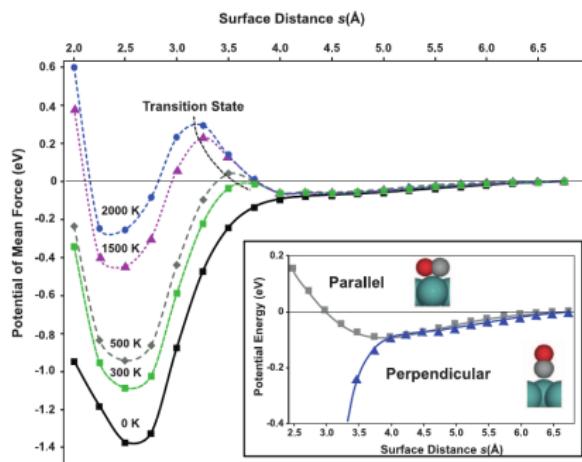
As is to be expected from negligible barrier in potential of mean force (PMF)



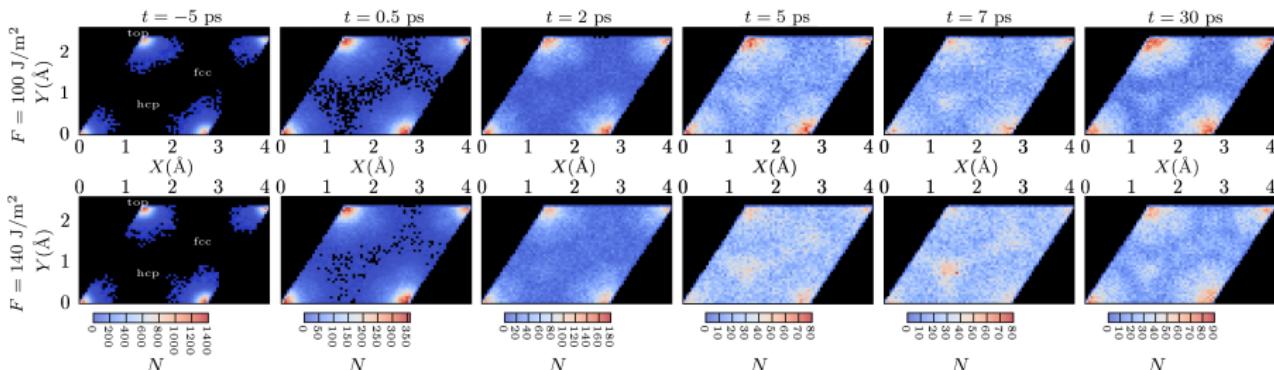
# Why are the entropic barriers of the PMFs so different?

Because separability assumption fails clearly

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

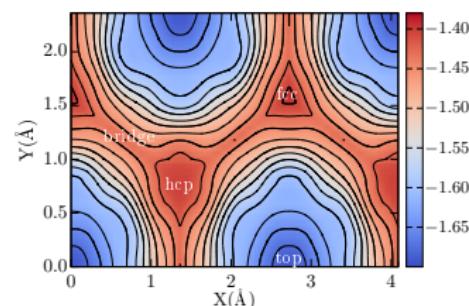


# Dynamical trapping: alternative/additional explanation?

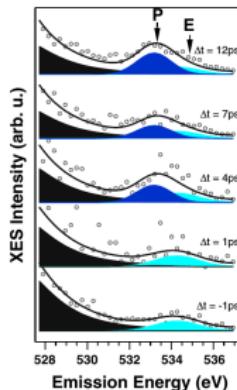
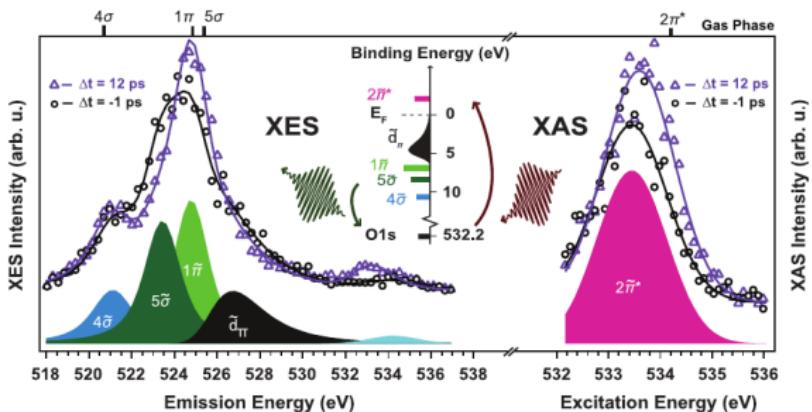


## Surprising patterns in XY-distribution

- 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 computed:  $2\pi^*$ -intensity not increased
- 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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