

# 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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## 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 time for any first questions)

## 3 Results

# Outline

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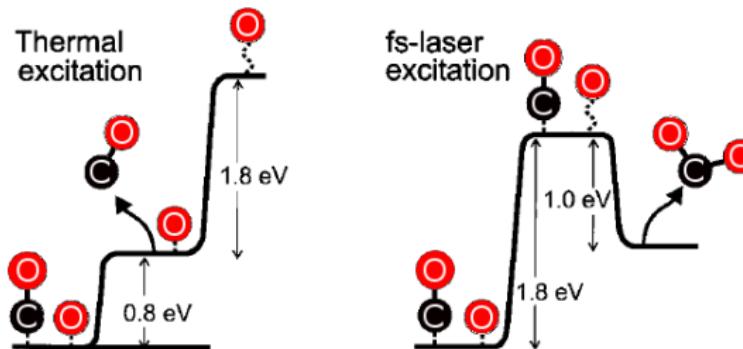
3

## Results

# 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



CO/O-coadsorbate @ Ru(0001)

M. Bonn *et al.*, Science 1999

# Specific motivation for the CO/Ru-System

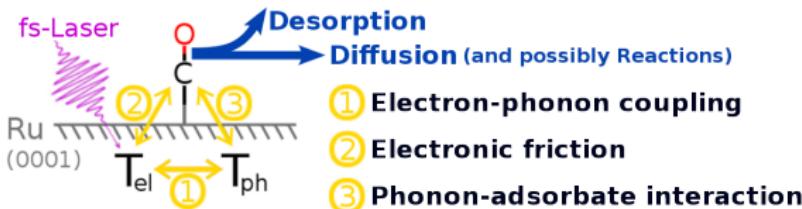
CO/Ru system important for catalysis

e. g. Fischer-Tropsch synthesis

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).
- recently, time resolved x-ray spectra (XAS and XES)  
⇒ “movie” of changes in orbital DOS

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



Coupling between three different kinds of degrees of freedom:

- electron gas ( $T_{el}$ )
  - initially absorbs laser energy
  - low heat capacity  $\Rightarrow$  high temperatures ( $\approx 5\text{-}10\text{ kK}$ )
- lattice vibrations ( $T_{ph}$ )
- adsorbate movement ( $T_{ads}$ )

# Details of the time-resolved x-ray experiment

Dell'Angela et al., *Science* 2013 (including Nilsson group, SLAC, Stanford)

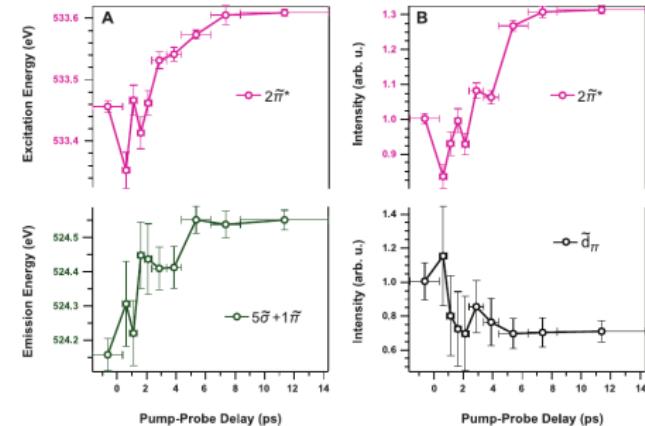
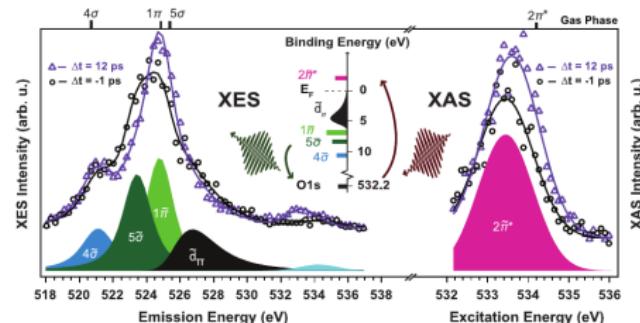
## What was done?

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

## What is observed?

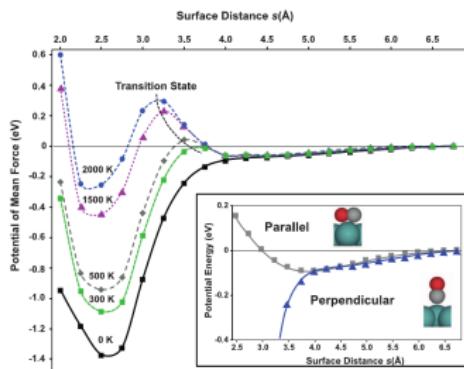
- orbital density of states at O
- energies shift towards gas-phase values of CO
- intensities change
  - $2\tilde{\pi}^*$   $\Rightarrow$  increase by  $\sim 30\%$
  - $\tilde{d}_\pi$   $\Rightarrow$  decrease by  $\sim 30\%$
  - participator peak appears

$\Rightarrow$  physisorbed precursor(?)



# Details of the accompanying theory

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



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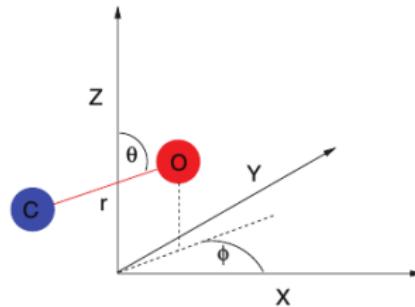
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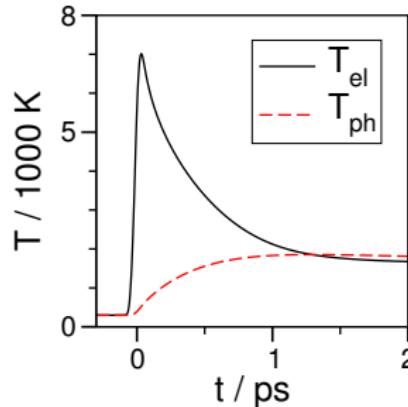
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# Ab-initio-based, full-dimensional (6D) potential energy surface (PES)

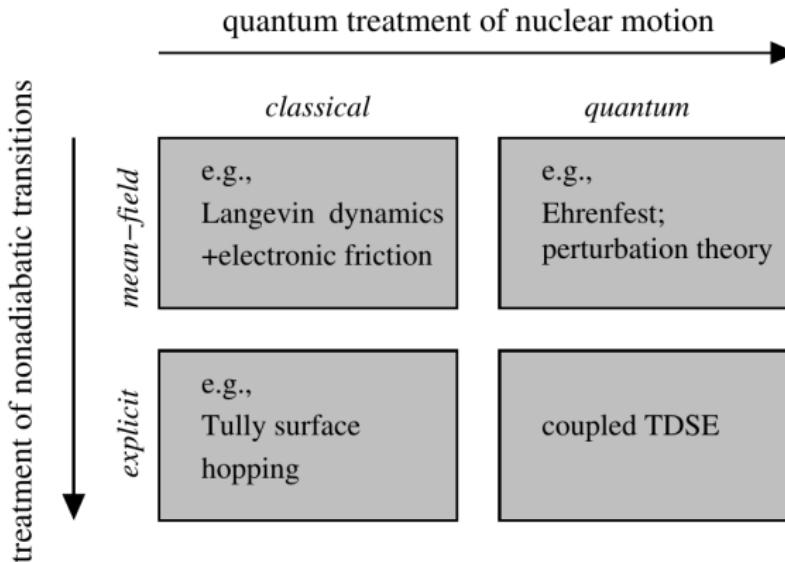


# Two-Temperature Model (TTM)

$$C_{\text{el}} \frac{\partial T_{\text{el}}}{\partial t} = \frac{\partial}{\partial z} \kappa \frac{\partial}{\partial z} T_{\text{el}} - g(T_{\text{el}} - T_{\text{ph}}) + S(z, t),$$
$$C_{\text{ph}} \frac{\partial T_{\text{ph}}}{\partial t} = g(T_{\text{el}} - T_{\text{ph}}).$$



# Non-adiabatic coupling



# Langevin Dynamics

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

- $R_{\text{el},k}(t)$  = Gaussian white noise
  - describes excitation by hot electron-hole pairs
  - dependent on:  $\eta_{\text{el},k}(\underline{r}_k)$  and  $T_{\text{el}}$

# Local density friction approx. plus independent atoms

# Generalized Langevin Oscillator

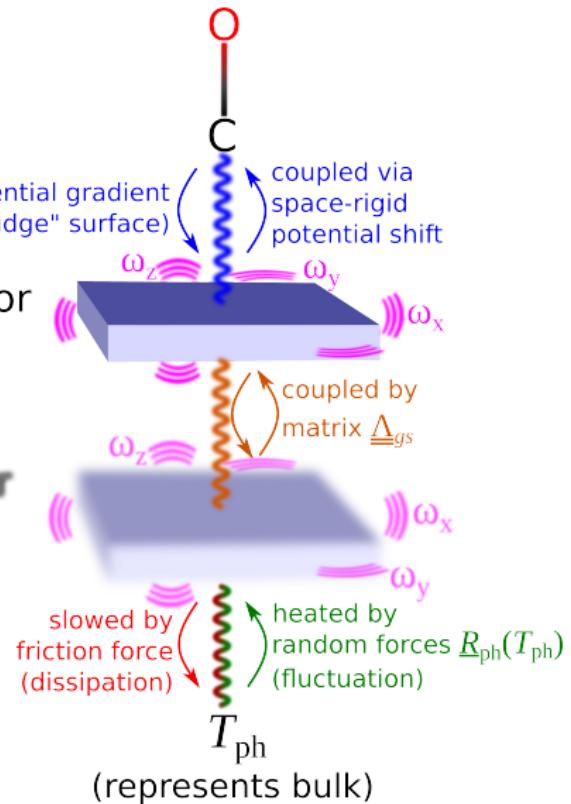
$$m_s \frac{d^2 r_s}{dt^2} = -\underbrace{\nabla_s V(r_1 - r_s, r_2 - r_s)}_{\text{Force due to PES}} - m_s \underbrace{\underline{\underline{\Omega}}^2 r_s}_{\text{Harmonic oscillator}} + m_s \underbrace{\underline{\underline{\Lambda}}_{gs} r_g}_{\text{Coupling to ghost oscillator}}$$

$$m_s \frac{d^2 r_g}{dt^2} = -m_s \underbrace{\underline{\underline{\Omega}}^2 r_g}_{\text{Harmonic oscillator}} + m_s \underbrace{\underline{\underline{\Lambda}}_{gs} r_s}_{\text{Coupling to surface force oscillator}} - \eta_{ph} \frac{dr_g}{dt} + R_{ph}(T_{ph})$$

Surface oscillator

both oscillate in the 3 dimensions x, y, z

Ghost oscillator



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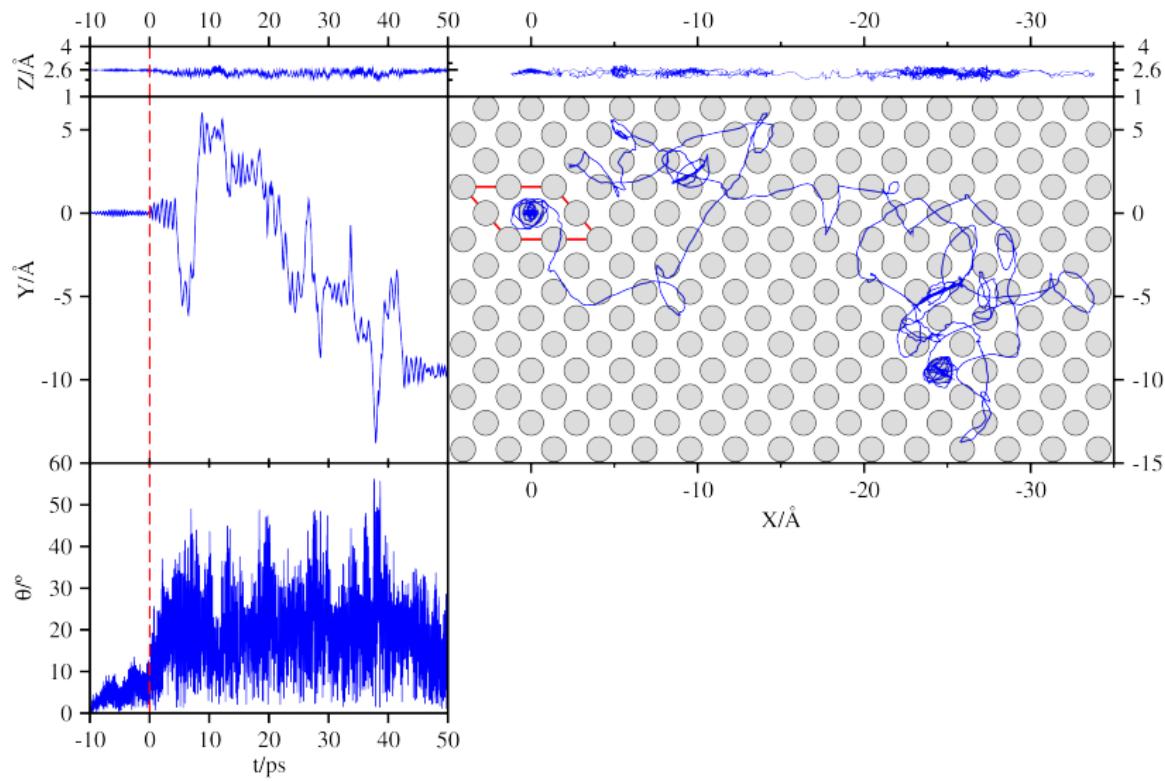
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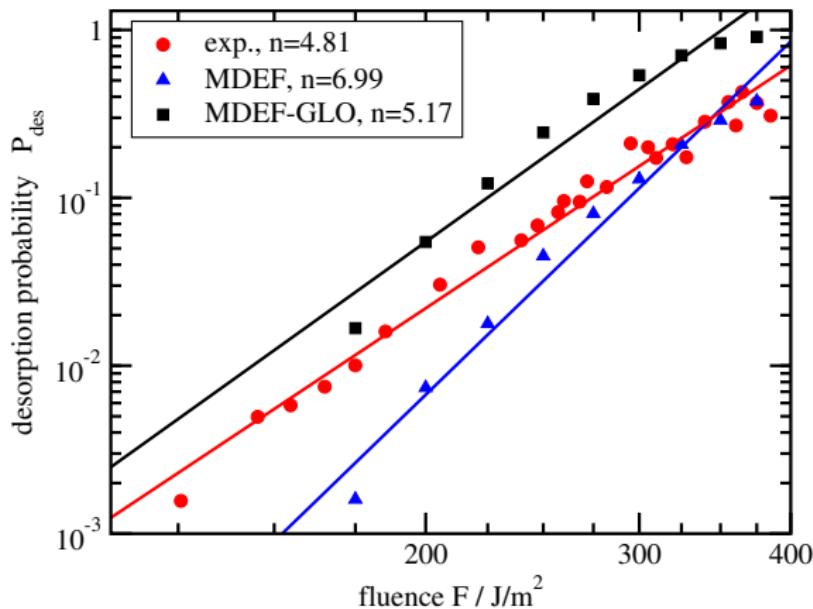
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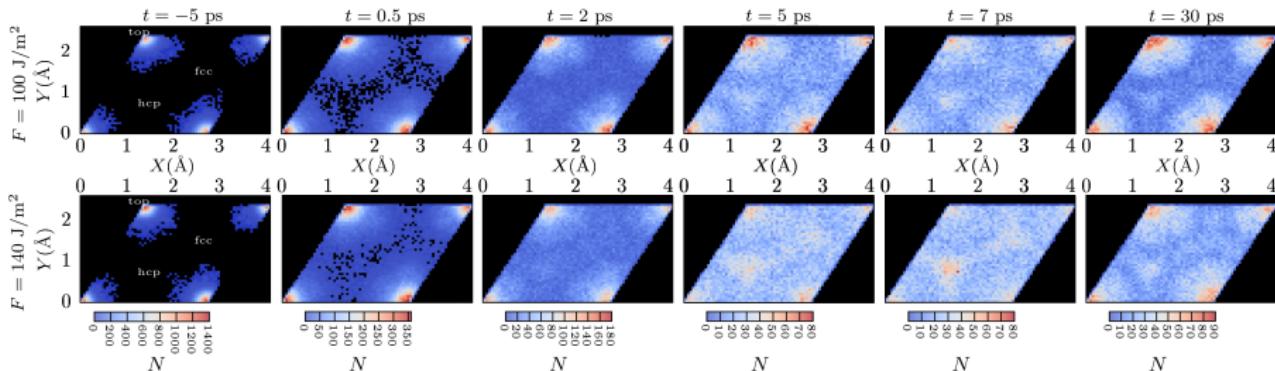
# Laser-Driven Diffusion



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



# Anisotropic diffusion + dynamical trapping



## 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)

