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
   - Laser-driven desorption
   - Physisorbed precursor states?
4. Summary and Outlook

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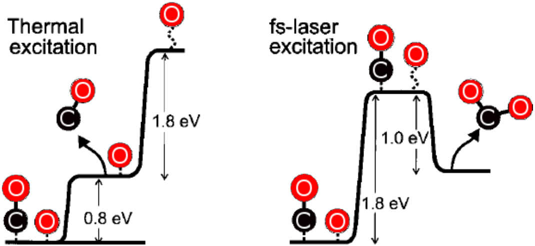
General motivation

Why investigate fs-laser-driven surface dynamics?

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



CO/O-coadsorbate @ Ru(0001)

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

Specific motivation for investigating CO/Ru(0001)

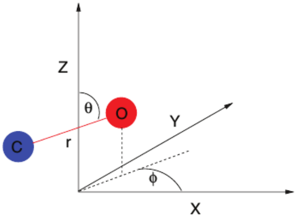
CO/Ru(0001) system important for catalysis, e.g.:

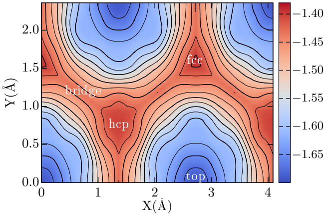
- Fischer-Tropsch synthesis
- exhaust gas converters (systems with similar metals)

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 preconstucted

$\Longrightarrow$ **enables large-scale dynamics!**

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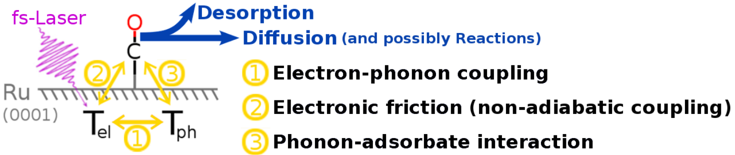
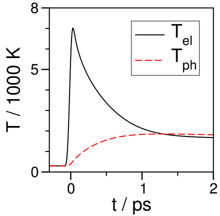
What happens after fs-laser excitation of the metal?



Coupling between 3 kinds of degrees of freedom:

- electron gas (T_{el})
  - initially absorbs laser energy
  - low heat capacity $\Rightarrow$ high T_{el} ($\approx$5-10 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)

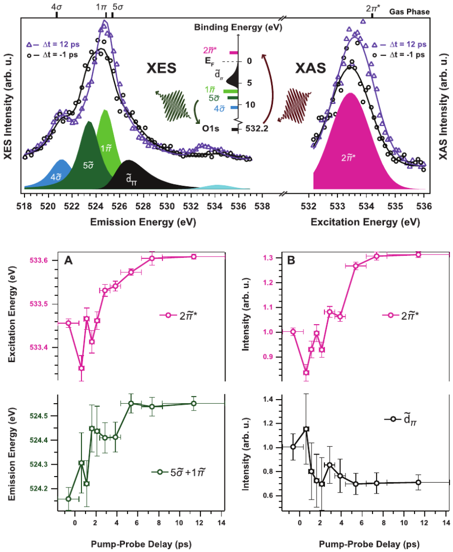
What was done?

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

What is observed?

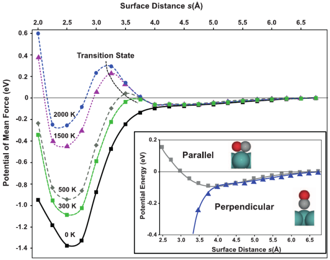
- orbital density of states at O
- energies shift towards gas-phase values of CO
- intensities change
  - $2\tilde{\pi}^*$ $\Rightarrow$ increase by $\sim 30\%$
  - $\tilde{d}_\pi$ $\Rightarrow$ decrease by $\sim 30\%$
  - participator peak appears

$\Rightarrow$ 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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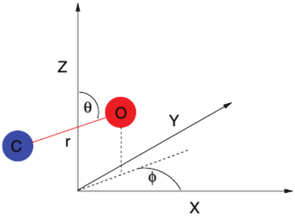
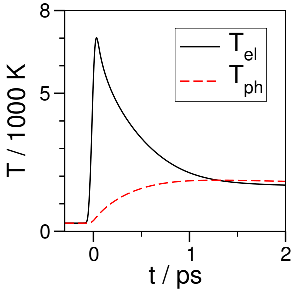
Ab-initio-based, full-dimensional (6D) potential energy surface (PES)



Two-temperature model (TTM)

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



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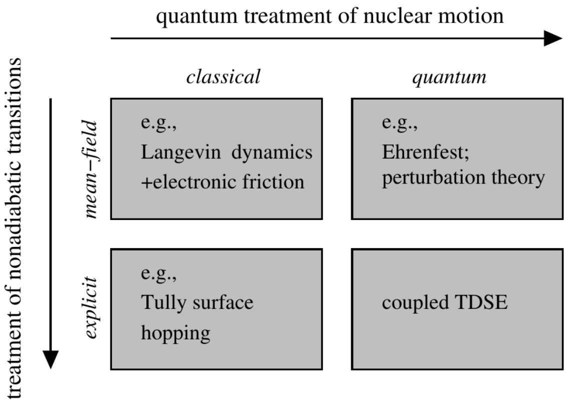
Different approaches to describe non-adiabatic coupling



Langevin Dynamics

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

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

Local density friction approx. plus independent atoms

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Generalized Langevin Oscillator

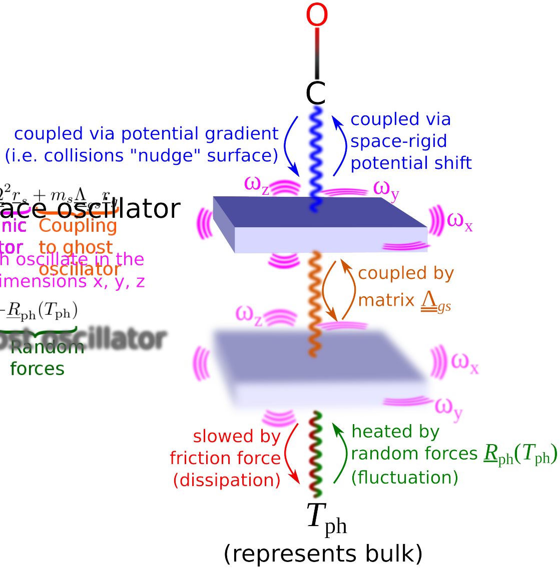
Surface oscillator

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

both oscillate in the 3 dimensions x, y, z

Ghost oscillator

$$m_s \frac{d^2\underline{r}_g}{dt^2} = \underbrace{-m_s \underline{\underline{\Omega}}^2 \underline{r}_g}_{\text{Harmonic oscillator}} \underbrace{+ m_s \underline{\underline{\Lambda}}_{gs} \underline{r}_s}_{\text{Coupling to surface oscillator}} \underbrace{-\eta_{\text{ph}} \frac{d\underline{r}_g}{dt}}_{\text{Friction force}} \underbrace{+\underline{R}_{\text{ph}}(T_{\text{ph}})}_{\text{Random forces}}$$



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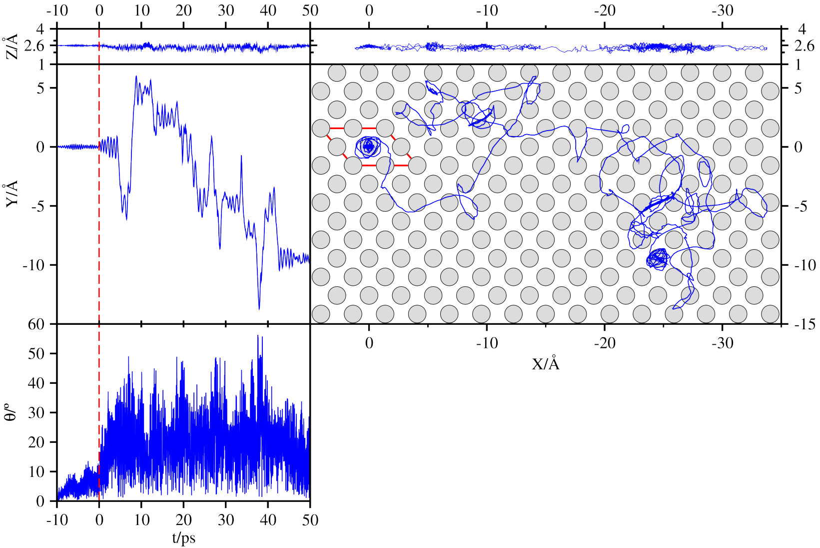
Example trajectory
(in this case without GLO-model)



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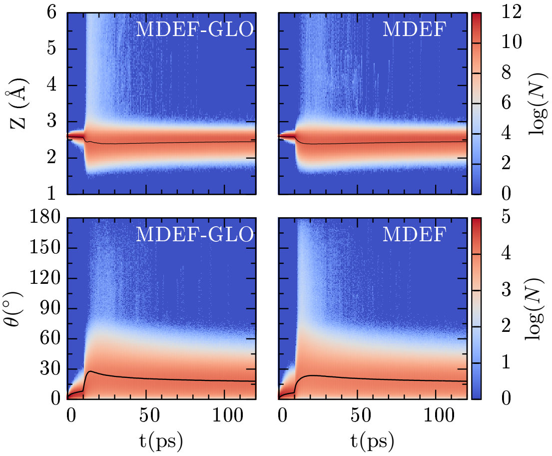
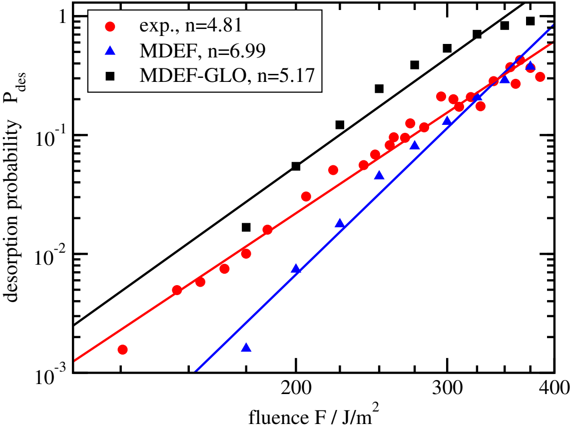
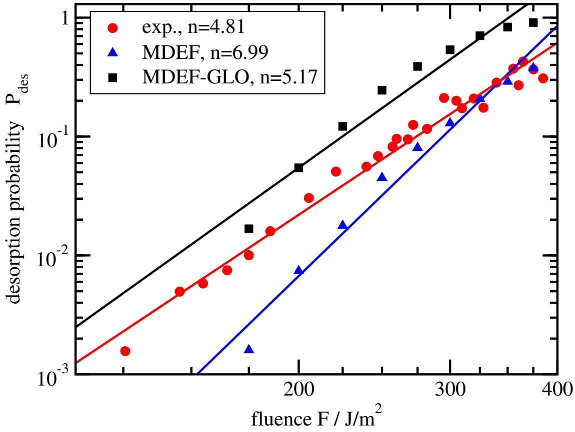
Heating of DOFs Z and θ



Fluence-dependence of desorption yield P_{des}



Two-pulse correlation of desorption



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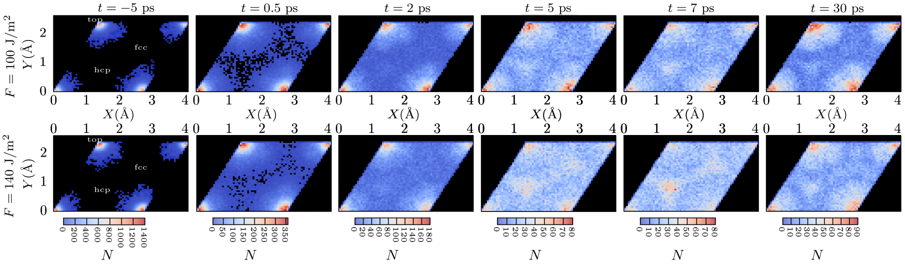
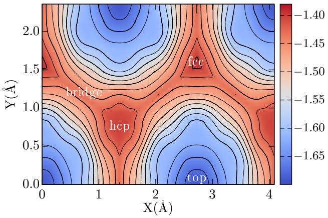
Anisotropic diffusion patterns + dynamical trapping



Suprising patterns in XY-distribution

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



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